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(54) **Ink-jet recording material with improved light-resistance**

(57) An ink jet recording material including a specific light fastness-enhancing agent coated on or impregnated in a support material and including at least one member selected from hydroquinone, hydroquinone derivatives, pyrocatechol derivatives, and phenol compounds having one or more sulfonate groups, the specific light fastness-enhancing agent enabling ink images recorded on the recording sheet to exhibit an enhanced light fastness.

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to an ink jet recording material. More particularly, the present invention relates to an ink jet recording material capable of enhancing the light fastness of ink images recorded thereon.

2. Description of the Related Art

[0002] An ink jet recording system, in which an aqueous ink is jetted imagewise through a fine opening of a jetting nozzle toward a recording material to form ink images, is advantageous in that printing noise is low, full colored images can be easily recorded, the recording can be effected at a high speed, and the ink jet printer is cheaper than other printers, and thus the application of the ink jet recording system has progressed in many fields including, for example, terminal printers for computers, facsimile machines, plotters, and book and slip printers.

[0003] Currently, since the use of the ink jet printer has been rapidly expanded and the quality of the printed images has been improved, the ink jet recording material is strongly required not only to have a good appearance but also to be capable of imparting a high stability to the ink images recorded thereon, particularly a high resistance of the recorded ink images to light. However, since the inks for the ink jet recording system must satisfy requirements of not blocking the ink jet nozzle and of having a brilliant hue, the inks are not always selected from pigment inks and dye inks having a high light fastness.

[0004] To solve the above-mentioned problems, a plurality of attempts for enhancing the light fastness of ink images printed on the ink-jet recording material by adding various resistance-enhancing materials to the recording material. For example, Japanese Unexamined Patent Publication No. 57-87,988 discloses an ink jet recording sheet containing, as at least one component, an ultraviolet ray-absorbing agent. Japanese Unexamined Patent Publication No. 61-146,591 discloses an ink jet recording medium usable for recording images thereon by using an aqueous ink containing a water-soluble dye, characterized by containing therein a hindered amine compound. Japanese Unexamined Patent Publication No. 4-201,594 discloses a recording material comprising a base material and an ink receiving layer formed on the base material and characterized in that the ink receiving layer contains super fine particles of transition metal compounds. The above-mentioned recording materials exhibit, to a certain extent, a light fastness-enhancing effect for the ink images recorded thereon. However, they are disadvantageous in that the recording materials exhibit a poor ink-absorbing property, the light fastness-enhancing effect is insufficient for practice and after fading, the faded colors are badly balanced.

[0005] Also, Japanese Unexamined Patent Publication No. 61-57,380 discloses an ink jet recording medium for recording thereon ink images formed by using an aqueous ink containing a water-soluble dye, characterized in that the recording medium contains a porous inorganic pigment, a cationic resin and a magnesium compound having a very poor water solubility. Japanese Unexamined Patent Publication No. 57-87,987 discloses an ink jet recording sheet for recording thereon images formed from an ink containing an acid dye or a mordant dye, comprising at least one member selected from molybdic acid and tannic acid and contained in or coated on a base sheet. They can enhance the light fastness of the ink images recorded thereon, but the enhanced light fastness may not be sufficient. However, when the printed sheet is stored for a long time, the light fastness of the recorded ink images is insufficient, and the molybdic acid is unsatisfactory in that after fading, the color balance is lost, and the non-printed portions of the recording sheet become discolored.

[0006] Accordingly, an ink jet recording material free from the above-mentioned disadvantages is in strong demand.

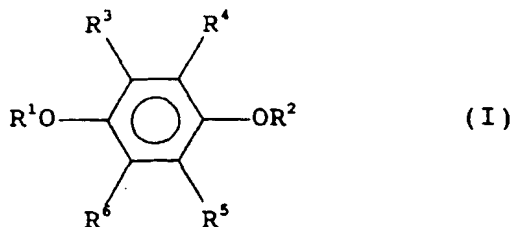
SUMMARY OF THE INVENTION

[0007] An object of the present invention is to provide an ink jet recording material providing high light fastness to ink images recorded thereon.

[0008] The above-mentioned object can be attained by the ink jet recording material of the present invention which comprises a support material and a light fastness-enhancing agent (a light resistant agent) for ink images received on the recording material, comprised in the support material, and comprising at least one member selected from the group consisting of hydroquinone, hydroquinone derivatives, pyrocatechol derivatives and phenol compounds having at least one sulfonate group.

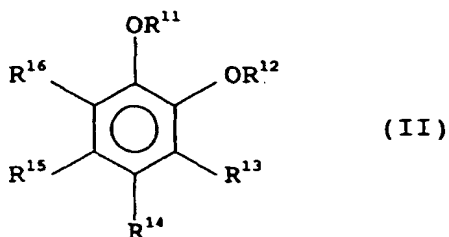
[0009] In the ink jet recording material of the present invention,

(1) the hydroquinone derivatives are preferably selected from those represented by the general formula (I):



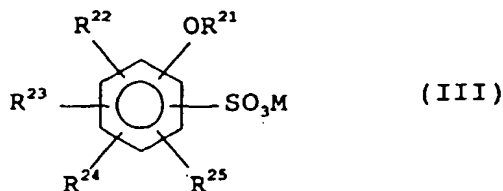
15 wherein R^1 and R^2 respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups, and $-R^7\text{-COOH}$ groups wherein R^7 represents a hydrocarbon group; R^3 , R^4 , R^5 and R^6 respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a sulfonic acid group, a sulfonate salt group, a carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups and aralkyl groups, and R^3 and R^4 and R^5 and R^6 respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; at least one of R^1 to R^6 is not a hydrogen atom; and the saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups and $-R\text{-COOH}$ groups represented by R^1 to R^2 and the alkyl groups, aryl groups and aralkyl groups represented by R^3 , R^4 , R^5 and R^6 each may have at least one substituent,

20 (2) the pyrocatechol derivatives are preferably selected from those represented by the general formula (II):



35 wherein R^{11} and R^{12} respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups, and $-R^{17}\text{-COOH}$ groups wherein R^{17} represents a hydrocarbon group; R^{13} , R^{14} , R^{15} and R^{16} respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a sulfonic acid group, a sulfonate salt group, a carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups and aralkyl groups, and R^{13} and R^{14} and R^{15} and R^{16} respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; and the saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups and $-R\text{-COOH}$ groups represented by R^{11} to R^{12} and the alkyl groups, aryl groups and aralkyl groups represented by R^3 , R^4 , R^5 and R^6 each may have at least one substituent, and

40 (3) the phenol compounds having at least one sulfonate group ($-\text{SO}_3^-$) are preferably selected from those represented by the general formula (III):



wherein R^{21} represents a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups and alkyl groups; R^{22} , R^{23} , R^{24} and R^{25} respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a hydroxyl group, - SO_3M groups, a carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups, and aralkyl groups; R^{22} and R^{23} and R^{24} and R^{25} respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; the saccharose residues, aryl groups, acyl groups, aralkyl groups and alkyl groups represented by R^{21} and the alkyl groups, aryl groups and aralkyl groups may have at least one substituent; and M represents a member selected from the group consisting of a hydrogen atom, metal atoms, an ammonium group and cationic organic groups.

[0010] In the ink jet recording material of the present invention, hydroquinone- β -D-glucoside is preferably employed as a hydroquinone derivative; the pyrocatechol derivatives are preferably selected from salts of pyrocatechol-3,5-disulfonic acid, for example, disodium pyrocatechol-3,5-disulfonate; and the hydroxyaryl compounds having at least one sulfonic group are preferably selected from salts of phenol sulfonic acid and salts of sulfo-salicylic acid.

[0011] In the ink jet recording material of the present invention, the light fastness-enhancing agent may be comprised in the support material by impregnating an impregnation liquid containing the light fastness-enhancing agent in the support material and drying; or by coating a coating liquid containing the light fastness-enhancing agent on the support material and drying.

[0012] The ink jet recording material optionally further comprises an inorganic pigment which is preferably porous, and/or a cationic resin comprised in the support material, to enhance an ink absorbing property and/or a water resistance of recorded ink images. The porous inorganic pigment, in the form of fine particles having an average particle size of 1 μ m or less, contributes to enhancing the quality of recorded ink images on the recording material.

[0013] In the ink jet recording material of the present invention, at least one ink receiving layer containing the light fastness-enhancing agent may be formed on at least one surface of the support material. The ink receiving layer contributes to improving the quality of ink images recorded on the recording material.

[0014] Preferably, the ink receiving layer contains the light fastness-enhancing agent and a pigment.

[0015] The ink receiving layer containing the light fastness-enhancing agent can be formed on the support material in such a manner that a layer containing the light fastness-enhancing agent is formed on a casting surface of a casting base, and then is brought into contact with a surface of the support material under pressure so as to transfer the cast layer to the support material surface, and the cast layer on the support material is separated from the casting surface of the casting base.

[0016] In the ink jet recording material of the present invention, the inorganic pigment preferably comprises a plurality of particles of at least one member selected from the group consisting of silica, alumina and aluminosilicate.

[0017] In the ink jet recording material of the present invention, the inorganic pigment preferably comprises a plurality of secondary particles having an average particle size of 10 to 500 nm, each secondary particle comprising a plurality of primary particles having an average primary particle size of 3 to 40 nm, and agglomerated with each other to form a secondary particle.

[0018] The ink jet recording material of the present invention preferably has a gloss of 20% or more determined at an incident angle of 75 degrees in accordance with Japanese Industrial Standard P8142.

[0019] The ink jet recording material of the present invention optionally further comprises at least one inorganic salt.

[0020] The inorganic salt is preferably selected from salts of di- or more valent metals. The di- or more valent metal salts are preferably selected from the group consisting of magnesium salts and calcium salts.

[0021] The ink jet recording material of the present invention optionally, further comprises at least one member selected from the group consisting of salts of phosphoric acids and salts of nitric acid. The phosphoric acid salts are preferably selected from the group consisting of salts of glycerophosphoric acid and metaphosphoric acid.

[0022] Also, the phenol compounds having at least one sulfonate group and usable for the present invention refers to aromatic compounds having at least one hydroxyaryl structure, for example, phenol and naphthol structures and others, substituted with at least one sulfonate ($-SO_2O-$) group.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] The ink jet recording material may have an appearance similar to that of a woodfree paper sheet, a coated paper sheet or a gloss-coated paper sheet.

[0024] The woodfree paper sheet-like recording material refers to a recording sheet having an appearance similar to that of a plain paper sheet having no coating layer and can be produced by impregnating a support material, for example, a woodfree paper sheet, with a liquid containing the specific light fastness-enhancing agent for the recorded ink images and drying. The impregnation can be effected by immersing the support material in the impregnation liquid,

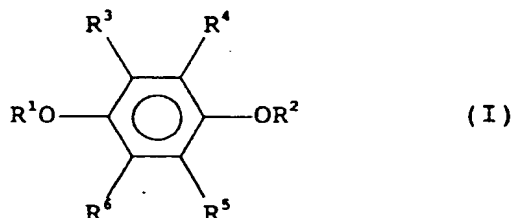
taking out the immersed material from the impregnation liquid and drying the impregnated material, or by coating the support material with the impregnation liquid, allowing the impregnation liquid to penetrate into the inside of the support material and drying the coated material. The impregnation liquid may optionally contain a resin, a sizing agent and/or a pigment as long as the resultant impregnation liquid can penetrate into the inside of the support material. Usually, the impregnation liquid is applied in a total dry amount of 5 g/m² on both surfaces of the support material.

[0025] The ink jet recording material having an appearance similar to that of a coated paper sheet comprises a support material, for example, a paper sheet, a synthetic paper sheet, a film or a resin-coated paper sheet, and coating layers (ink receiving layers) formed on the support material and comprising a pigment, a binder resin and a light fastness-enhancing agent. Each ink receiving layer may be formed in multi-layers.

[0026] The ink jet recording material having an appearance similar to that of a gloss coated paper sheet has at least one gloss layer by which at least one outermost gloss surface of recording material is formed. In an embodiment, the gloss layer comprises, as a principal component, a resin and in another embodiment, the gloss layer comprises, as a principal component, fine pigment particles having a particle size of 1.0 µm or less. Optionally, an undercoat layer is formed between the support material and the upper gloss layer. The gloss layer can be formed by a film transfer method or a cast method.

[0027] The ink jet recording material of the present invention comprises a light fastness-enhancing agent, for ink images recorded on the recording material, comprised in the support material. The light fastness-enhancing agent comprises at least one member selected from (1) hydroquinone and hydroquinone derivatives, (2) pyrocatechol derivatives and (3) phenol compounds having at least one sulfonate group presented by the formula: -SO₂O-.

[0028] The hydroquinone derivatives are preferably selected from those represented by the general formula (I):

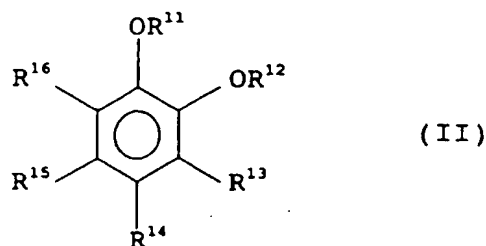


wherein R¹ and R² respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups, and -R⁷-COOH groups wherein R⁷ represents a hydrocarbon group; R³, R⁴, R⁵ and R⁶ respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom a sulfonic acid group, a sulfonate salt group, carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups and aralkyl groups, and R³ and R⁴ and R⁵ and R⁶ respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; and at least one of R¹ to R⁶ is not a hydrogen atom. The saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups and -R-COOH groups represented by R¹ to R² and the alkyl groups, aryl groups and aralkyl groups represented by R³, R⁴, R⁵ and R⁶ each may have at least one substituent selected from, for example, alkyl, sulfonic acid and carboxylic acid groups.

[0029] Preferably, R¹ and R² respectively represent a member selected from a hydrogen atom, saccharose residues, for example, a glucose residue, aryl groups, for example, a phenyl group, and a naphthyl group, and aralkyl groups, for example, a benzyl group and a phenylethyl group, acyl groups, for example, an acetyl group and a C₂H₅O-group, and alkyl groups, for example, C₁ to C₂₀ alkyl groups.

[0030] Preferably, R³, R⁴, R⁵ and R⁶ respectively represent a member selected from a hydrogen atom, a sulfonic acid group and sulfonate salt groups, for example, a sodium sulfonate group and a potassium sulfonate group.

[0031] The pyrocatechol derivatives are preferably selected from those represented by the general formula (II):

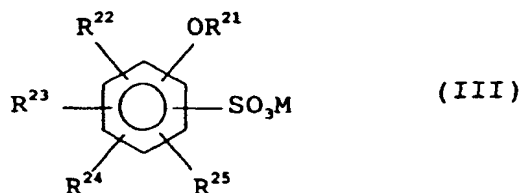


wherein R¹¹ and R¹² respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups, and -R¹⁷-COOH groups wherein R¹⁷ represents a hydrocarbon group; R¹³, R¹⁴, R¹⁵ and R¹⁶ respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a sulfonic acid group, a sulfonate salt group, carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups and aralkyl groups, and R¹³ and R¹⁴ and R¹⁵ and R¹⁶ respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group. The saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups and -R-COOH groups represented by R¹¹ to R¹² and the alkyl groups, aryl groups and aralkyl groups represented by R¹³, R¹⁴, R¹⁵ and R¹⁶ each may have at least one substituent selected from, for example, sulfonic acid and carboxylic acid groups.

[0032] Preferably, R¹ to R² respectively represent a member selected from a hydrogen atom, saccharose residues, for example, a glucose residue, and alkyl groups, for example, C₁ to C₂₀ alkyl groups.

[0033] Preferably, R¹³, R¹⁴, R¹⁵ and R¹⁶ respectively represent a member selected from a hydrogen atom, a sulfonic acid group and sulfonate salt groups, for example, a sodium sulfonate group and a potassium sulfonate group, a carboxylic acid group, and carboxylate salt groups, for example, a sodium carboxylate and a potassium carboxylate group.

[0034] The phenol compounds having at least one sulfonate group (-SO₃⁻) are preferably selected from those represented by the general formula (III):



wherein R²¹ represents a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups and alkyl groups; R²², R²³, R²⁴ and R²⁵ respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a hydroxyl group, -SO₃M groups, a carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups, and aralkyl groups; R²² and R²³ and R²⁴ and R²⁵ respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; the saccharose residues, aryl groups, acyl groups, aralkyl groups and alkyl groups represented by R²¹ and the alkyl groups, aryl groups and aralkyl groups may have at least one substituent selected from, for example, sulfonic acid and carboxylic acid groups; and M represents a member selected from the group consisting of a hydrogen atom, metal atoms an ammonium group and cationic organic groups, preferably, alkali metals, alkaline earth metals, heavy metals, more preferably alkali metals.

[0035] In the phenol compounds represented by the formula (III), one of the -SO₃M groups is preferably located in a para-position with respect to the -OR²¹ group.

[0036] Preferably, R²¹ represents a hydrogen atom.

[0037] Preferably, R²², R²³, R²⁴ and R²⁵ respectively and independently from each other represent a hydrogen atom, a SO₃M group, a carboxylate salt group, or a carboxylic acid group.

[0038] The hydroquinone and hydroquinone derivatives are preferably selected from hydroquinone, hydroquinone-β-D-glucoside (namely arbutin), hydroquinone-monobenzylether, hydroquinone diacetate, hydroquinone monomethylether, hydroquinone dimethylether, hydroquinone monoethylether, hydroquinone-monosulfonic acid salts, for example, potassium hydroquinonesulfonate, hydroquinone, hydroquinone disulfonic acid salts, for example, dipotassium hydro-

quinone-2,5-disulfonate, hydroquinone mono-n-hexyl-ether, and hydroquinone monophenylether. The arbutin exhibits an excellent light fastness-enhancing effect on the recorded ink images.

[0039] The reason the light fastness of the recorded ink images is enhanced to an great extent by the specific light fastness-enhancing agent of the present invention has not yet been completely made clear. It is assumed that the coloring dyes or pigments contained in the inks for the ink jet recording system and exhibiting a low light fastness when directly exposed to light, are protected by the light fastness-enhancing agent contained in the recording material from the light by a certain mechanism. This mechanism has not yet been made clear.

[0040] There is no limit to the amount of the hydroquinone and/or hydroquinone derivatives to be comprised in the recording material. Generally, the hydroquinone and/or hydroquinone derivatives are preferably comprised in an amount of 0.01 to 5g more preferably 0.01 to 2g, per m² of the area of each surface of the recording material. When the content of the hydroquinone and/or hydroquinone derivatives is less than 0.01 g/m², the resultant recording material may exhibit an unsatisfactory light fastness for the recorded ink images. Also, if the content is more than 2 g/m², the light fastness-enhancing effect on the resultant recording material may be saturated and no further enhancement on the light fastness can be expected.

[0041] The pyrocatechol derivatives usable as a light resistant material for the present invention, is preferably selected from, for example, pyrocatecholsulfonphthalein, pyrocatechol-3,5-disulfonic acid salts, pyrocatecholdimethyl-ether (namely veratrole), pyrocatecholmonoethylether, catechol-antimony complex, catechol-3-carboxylic acid, catechol-4-carboxylic acid, catechol complexes, sodium catecholacetate, and catechol-3,6-dicarboxylic acid. Among the above-mentioned compounds, the pyrocatechol-3,5-disulfonic acid salts are more preferably employed for the present invention. None-modified catechol exhibit a certain light fastness for the recorded ink images. However, the high resistance of pyrocatechol is lower than that of the pyrocatechol derivatives as mentioned above. Particularly the pyrocatechol derivatives having a glucoside group, sulfonate group and acetate group are preferred for the present invention.

[0042] The pyrocatechol-3,5-disulfonic acid salts exhibit an excellent light fastness-enhancing effect and, particularly, disodium pyrocatechol-3,5-disulfonate is preferred.

[0043] In the recording material of the present invention, it is assumed that the pyrocatechol derivatives can stabilize or protect, using an unknown mechanism, the ink images which, per se, exhibit a poor resistance to fading by light.

[0044] The pyrocatechol derivatives are preferably contained in an amount of 0.01 to 5g, more preferably 0.01 to 2g, per m² of area of a surface of the recording material. When the amount is less than 0.01 g/m², the resultant recording material may exhibit an unsatisfactory light fastness-enhancing effect, and when the amount is more than 5 g/m², the light fastness enhancing effect may be saturated and an economical disadvantage may occur.

[0045] The phenol compounds having at least one sulfonate group are usable as a light fastness-enhancing agent for the present invention. The term "phenol compounds having at least a sulfonate group" refer to hydroxyaryl compounds, for example, hydroxyphenyl and hydroxynaphthyl compounds, having at least one sulfonate (-SO₂O-) group.

[0046] The sulfonate group-containing phenol compounds usable for the present invention are preferably selected from phenolsulfonic acid salts, sulfosalicylic acid salts, hydroquinonesulfonic acid salts, hydroquinonedisulfonic acid salts, pyrocatecholdisulfonic acid salts, naphtholsulfonic acid salts and naphtholdisulfonic acid salts. Among these compounds, the phenolsulfonic acid salts and the sulfosalicylic acid salts are particularly preferred for the present invention. The salts include sodium salts.

[0047] It is assumed that, in the recording material of the present invention, the phenol compounds having at least one sulfonate group stabilize or protect, using an unknown mechanism, the recorded dye or pigment ink images which, per se, exhibit a poor light fastness.

[0048] There is no limitation to the content of the sulfonate group-containing phenol compounds in the recording material. Usually, the content is preferably 0.01 to 5g, more preferably 0.01 to 2g, per m² of area of the surface of the recording material. When the content of the sulfonate group-containing phenol compounds is less than 0.01 g/m², the resultant recording material may exhibit an unsatisfactory light fastness-enhancing effect, and when the content is more than 2 g/m², the light fastness-enhancing effect is saturated and the cost of producing the recording material may increase too much.

[0049] There is no limitation to the distribution of the light fastness-enhancing agent in the recording material. The light fastness-enhancing agent may be uniformly distributed throughout the recording material or locally distributed in the recording surface portions of the recording material.

[0050] The recording material of the present invention comprising the specific light fastness-enhancing agent may be produced by forming a paper sheet by a paper-forming procedure using a pulp slurry containing the specific light fastness-enhancing agent of the present invention; by forming a film by a film-forming procedure using a polymer melt or polymer solution containing the specific light fastness-enhancing agent of the present invention; by sizing a paper sheet with a sizing liquid containing the specific light fastness-enhancing agent; by impregnating a support material with an impregnation liquid containing the specific light fastness-enhancing agent; or by coating at least one surface of a support material with a coating liquid containing the specific light fastness-enhancing agent, while allowing the coating liquid to penetrate into the inside of the support sheet. In the above-mentioned methods, the resultant recording mate-

rial has an appearance similar to the woodfree paper sheet or a non-coated paper sheet. In the above-mentioned methods, the pulp slurry, film-forming material, sizing liquid, impregnation liquid or coating liquid optionally contains a cationic resin, an aqueous non-cationic resin or a pigment.

[0051] When the recording material is in the form similar to a coated paper sheet, at least one coating layer is coated on at least one surface of a support material to provide an ink receiving layer. The coating liquid for the ink receiving layer contains at least one material which allows the ink to be absorbed in the coating layer. When the coating layer is formed in multiple layers, at least an uppermost coating layer must contain the specific light fastness-enhancing agent. The light fastness-enhancing agent-containing layer may be formed from the specific light fastness-enhancing agent alone or a mixture of the specific light fastness-enhancing agent with at least one additive, for example, a binder and a pigment.

[0052] The ink-absorbing material for the ink receiving layer includes various pigments and hydrophilic polymers. When the pigments and hydrophilic polymers are employed together, the resultant recording material exhibits an enhanced water resistance, a good ink-absorbing rate, and a good ink-drying property. The ink-absorbing pigments and hydrophobic polymers may be contained in the inside of the supporting material, to form a woodfree paper sheet-like recording material. Preferably, the ink absorbing pigments and hydrophobic polymers are contained, as principal components, in the ink receiving layer formed on the support material.

[0053] The ink receiving layer may be formed from a water-soluble polymeric material and/or a water-dispersible polymeric material optionally mixed with a pigment.

[0054] The polymeric materials usable for the ink receiving layer preferably comprises at least one member selected from water-soluble polymeric materials, for example, polyvinyl alcohol, modified polyvinyl alcohols, for example, cation-modified polyvinyl alcohols and silyl-modified polyvinyl alcohols, natural polymeric materials, for example, gelatin, casein, soybean protein, starch and cationic starches, and cellulose derivatives, for example, carboxymethylcellulose, methylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and vinylpyrrolidone polymers and copolymers; hydrophilic, water-insoluble polymeric materials, for example, polyurethanes, polyesters, sodium polyacrylate, latices of vinyl copolymers, for example, latices of acrylic copolymers and latices of styrene-vinyl acetate copolymers, and aqueous dispersions of conjugated diene polymers and copolymers, for example, of styrene-butadiene copolymers and methyl methacrylate-butadiene copolymers. The above-mentioned polymeric materials can be employed as an ink-absorbing material to form, as a principal component, the ink receiving layer. In view of a high ink absorption, the polymeric materials for the ink receiving layer are preferably selected from the water-soluble polymeric materials.

[0055] The polymeric material may be employed as a binder component for forming an ink receiving layer comprising, as a principal component, as a pigment which will be explained later. In this case, there is no limitation to the mixing ratio of the pigment to binder. Usually, the mixing dry weight ratio of the pigment to the binder is preferably controlled to 100:2 to 100:200, more preferably 100:5 to 100:100. When the content of the binder is too high, the total volume of gaps formed between the pigment particles may become too small and thus the ink-absorbing rate of the resultant ink receiving layer may be unsatisfactory. Also, when the content of the binder is too low, the resultant ink receiving layer may exhibit an insufficient resistance to cracking and the resultant ink images recorded thereon may exhibit an unsatisfactory accuracy and color density.

[0056] When an ink receiving layer comprising, as a main component, the water soluble polymeric materials or the water-dispersible polymeric material, is formed on a support material, the resultant ink jet recording material exhibits an enhanced gloss. However, to enhance the ink absorption property, the ink receiving layer should contain the fine particles of the pigment in a high content. In the ink receiving layer containing, as a main component, the polymeric material, the pigment may be further contained. In this case, however, the pigment should be contained in a content of 10% by weight or less, preferably 5% by weight or less. The addition of the pigments contribute to enhancing the resistance of the resultant recording materials to blocking and to controlling the gloss of the resultant recording material.

[0057] The ink receiving layer may be a multi-layered ink receiving layer. When the uppermost layer of the ink receiving layer comprises, as a principal component, (1) a water-soluble polymeric material layer or (2) fine pigment particles having a particle size of 1 μm or less, the resultant ink jet recording material exhibits an enhanced gloss and high color density of the enhanced ink images.

[0058] Also, the lower layer in the multilayered ink receiving layer may be formed from, for example, the above-mentioned polymeric materials. Otherwise, the lower layer may be formed from a mixture of the polymeric material with the pigment particles having the above-mentioned particle size or "a particle size different from the above-mentioned particle size.

[0059] The pigments usable for the ink jet recording material of the present invention preferably comprise at least one member selected from porous inorganic pigments, for example, amorphous silica, colloidal silica, aluminosilicate, aluminum silicate, alumina, hydrated alumina, aluminum hydroxide, pseudo-boehmite, kaolin, clay calcined clay, calcined kaolin, zinc oxide, tin oxide, magnesium sulfate, calcium carbonate, satin white, magnesium silicate, magnesium carbonate, magnesium oxide, diatomaceous earth, and smectite; and fine particulate organic pigments, for example,

styrene polymer plastic pigments, urea resin plastic pigments, for example, urea-formaldehyde resin pigments, melamine-formaldehyde resin pigments, and benzoquanamine-formaldehyde resin pigments. For the recording material of the present invention, the inorganic pigments are preferably employed, particularly, amorphous silica, aluminosilicate, colloidal silica, and alumina are more preferably employed. More particularly, the amorphous silica and aluminosilicate pigments are more preferably employed.

[0060] When the ink receiving layer contains, as a principal component pigment particles having a particle size larger than 1 μm , for example, from 2 to 20 μm , the resultant ink jet recording material exhibit an excellent ink-absorbing property and is utilized for a mat grade (delustered) ink jet recording material.

[0061] For the use of forming images like silver salt photographic images, the ink receiving layer preferably comprises, as a principal component, pigment particles having a particle size or an agglomerated (secondary) particle size when the particles consists of agglomerates of fine primary particles, of 1 μm or less, more preferably 800 nm or less, still more preferably 600 nm or less. In this case, the resultant ink jet recording material exhibits an excellent ink-absorbing property and a high gloss and a high color density of the recorded ink images.

[0062] For example, the fine secondary particles of the pigment having an average secondary particle size of 1 μm or less can be prepared by applying a strong mechanical shearing force to a coagulated particles of the pigment having an average particle size of several μm and available in the trade. Namely, they can be produced from the trade-available coagulated pigment particles by a mechanical breaking-down method in which lumps of the coagulated pigment particles are finely pulverized. The mechanical breaking-down means include ultrasonic homogenizers, press-homogenizers, nanomizers, high speed rotation mills, roller mills, container-driving medium mills, medium-stirring mills, jet mills and sand grinders.

[0063] The term "average particle size" used in the present invention refers to an average of sizes (martin diameters) of particles determined by using an electron microscope (including SEM and TEM), unless specifically described otherwise. In the determination, "FINE PARTICLE HAND BOOK" published in 1991 by ASAKURA SHOTEN, page 52 was referred to. The martin diameters of particles located within an area of 5 cm \times 5 cm of a sample were measured by the electron microscope in a magnification of 10,000 to 400,000, and the average of the measured data was calculated.

[0064] In the present invention, the fine particles of the pigment having an average particle size of 1 μm or less are preferably selected from agglomerated particles.

[0065] The average particle size of the fine secondary particles of the pigment is preferably 1 μm or less, more preferably 800 nm or less still more preferably 600 nm or less, further more preferably 500 nm or less. This small particle size contributes to enhancing the gloss and the color density of the recorded ink images. The fine particle size of 500 nm or less corresponds to the particle size of colloidal particles. Most preferable range of the average particle size is from 20 nm to 300 nm.

[0066] The fine secondary particles of the pigment preferably comprise a plurality of primary particles having a primary particle size of 3 nm to 40 nm, more preferably 5 nm to 30 nm, still more preferably 10 to 20 nm.

[0067] For example, when amorphous silica particles having a secondary particle size of 500 nm or less and each comprising a plurality of primary particles having a primary particle size of 3 to 40 nm and agglomerated with each other, are selected as a pigment, and a recording material having at least an upper layer comprising the fine amorphous silica particles and formed on a support material is subjected to an ink jet printing, the resultant ink images exhibit a high gloss and a high color density of the images.

[0068] In a recording sheet having an appearance similar to a woodfree paper sheet or a coated paper sheet, a cationic polymeric material may be contained therein to enhance the fixing property of the ink applied thereon. The cationic polymeric material may be contained within the support material. Preferably, the recording material has one or more ink receiving layers formed on a supporting material and the cationic polymeric material is contained in at least an uppermost ink receiving layer. There is no limitation to the type of the cationic polymeric material. The cationic polymeric material includes various cationic polymeric compounds which produce water-insoluble salts with sulfon group or carboxyl group of dyes contained in the ink jet recording inks, and cationic resins containing secondary amines, tertiary amines and/or quaternary ammonium salts. Particularly, polyethyleneimines, polyvinyl pyridines, polyvinylamines, polymers of monoalkylamine-hydrochloric acid salts, polymers of diallylamine-hydrochloric acid salts, copolymers of monoallyl-amine-hydrochloric acid salts-diallylamine-hydrochloric acid salts, polymers of acrylamidealkyl tertiary ammonium salts, polyalkylenepolyamine-dicyanediimide condensation products, secondary amine-epichlorohydrin addition-polymerization products, and polyepoxyamines. The content of the cationic polymeric material in the recording material is preferably controlled in the range of from 0.01 to 10g per m^2 of the surface area of the recording material, more preferably from 0.1 to 5 g/m^2 .

[0069] The recording material or the ink receiving layer of the present invention optionally further comprises at least one additive selected from, for example, dispersing agents, viscosity-modifiers, anti-foaming agents, coloring materials, anti-static agents, and preservatives. Optionally, for the purpose of further enhancing the light fastness, the recording material or the ink receiving layer of the present invention further comprises a light stabilizer selected from, for example, ultraviolet ray absorbers, anti-oxidants, hindered amines, and other light stabilizers.

[0070] In an embodiment, the ink jet recording material of the present invention comprises an inorganic salt and a phenol compound.

[0071] There is no limitation to the type of the inorganic salts. Usually, the inorganic salt is preferably selected from sodium salts, magnesium salts, calcium salts, aluminum salts, phosphorus salts, titanium salts, iron salts, nickel salts, copper salts, and zinc salts. More preferably, the inorganic salt is selected from salts of di- or more valent metals, particularly magnesium salts and calcium salts, which contribute to enhancing the light fastness for the recorded ink images. Also, the inorganic salts preferably are selected from hydrochloric acid salts, sulfuric acid salts and phosphoric acid dihydrogen salts of the above-mentioned metals.

[0072] The phenol compounds include the above-mentioned specific phenol compounds. The phenol compounds are preferably selected from hydroquinone, hydroquinonesulfonic acid salts, hydroquinonedisulfonic acid salts, pyrocatechol, pyrocatechol-3,5-di-sulfonic acid salts (namely Tilon), hydroxybenzoic acid salts, sulfosalicylic acid salts, hydroxybenzenesulfonic acid salts, hydroquinone- β -D-glycoside (namely Arbutin) and naphthol compounds. The phenol compounds having one or more sulfonate groups, particularly hydroxybenzenesulfonic acid salts, sulfosalicylic acid salts and pyrocatechol-3,5-disulfonic acid salts exhibit an enhanced light fastness-enhancing effect on the recording material of the present invention.

[0073] It is assumed that the inorganic salts and the phenol compounds stabilize or protect the dyes contained in the ink jet recording inks which, per se, exhibit a poor light fastness, using an unknown mechanism, to significantly enhance the light fastness of the recorded ink images. Also, it is assumed that the phenol compounds having a phenolic hydroxyl groups contribute to preventing the reduction in the color density of the recorded images and the inorganic salts contribute to controlling the color balance of the images after fading.

[0074] There is no limitation to the contents of the inorganic salts and the phenol compounds. Usually, the contents of the inorganic salts and the phenol compounds in the recording material are respectively 0.01 to 2g per m² of the surface area of the recording material. When the contents are less than 0.01 g/m², the resultant recording material may exhibit an unsatisfactory light fastness. When the contents are more than 2 g/m², the light fastness-enhancing effect on the resultant recording material may be saturated. The inorganic salts and the phenol compounds may be coated alone or in a mixture thereof.

[0075] There is no limitation on the layer structure of the ink jet recording material comprising the inorganic salts and the phenol compounds. The recording sheet may be a paper sheet produced from a pulp slurry containing the inorganic salts and the phenol compounds by a paper-forming method, or a polymer film produced from a film-forming material mixed with the inorganic salts and the phenol compounds, or a paper sheet press-sized or impregnated with a liquid containing the inorganic salts and the phenol compounds, or a coated paper sheet produced by coating a paper sheet with a coating liquid containing the inorganic salts and the phenol compounds. These recording sheets have a woodfree paper-like appearance.

[0076] Preferably, at least one ink receiving layer comprising, as principal components, ink-absorbing materials is formed on a support material. In this case, a coated paper-like recording sheet is obtained. Preferably, at least an uppermost layer of the ink receiving layer contains the inorganic salts and the phenol compounds, or the uppermost layer is coated with a coating liquid containing the inorganic salts and the phenol compounds.

[0077] As a component of the ink receiving layer, various hydrophilic polymeric materials (resins) are employed, and, optionally, are mixed with pigments. In this case, a recording material having excellent water resistance, a good ink-absorption rate, and a good ink-drying property is obtained. The hydrophobic resin and optionally the pigment may be contained within the support material. In this case, the resultant recording material has an appearance similar to that of a woodfree paper sheet.

[0078] More preferably, the hydrophobic resins and optionally the pigments are contained, as principal components, in the ink receiving layer formed on a supporting material.

[0079] In another embodiment of the ink jet recording material of the present invention having an excellent light fastness, the specific phenol compounds as mentioned above are contained together with phosphoric acid salts and/or nitric acid salts in at least one layer of the ink receiving layer. The phosphoric acid salts include salts of sodium, potassium, calcium, magnesium, aluminum, zinc and nickel with metaphosphoric acid, tripolyphosphoric acid, 2-phosphoric acid, glycerophosphoric acid, hydrogen phosphoric acid, dihydrogen phosphoric acid, phosphorous acid, hydrogen phosphorous acid, guanidine-phosphoric acid, glucose-1-phosphoric acid, glucose-6-phosphoric acid, citidine-5'-1-phosphoric acid, citidine-5'-3-phosphoric acid, pyrophosphoric acid, hexafluorophosphoric acid and molybdophosphoric acid. The nitric acid salts include sodium nitrate, potassium nitrate, magnesium nitrate, cerium nitrate, yttrium nitrate and aluminum nitrate.

[0080] In view of balance between water resistance and light fastness, metaphosphoric acid salts, tripolyphosphoric acid salts, 2-phosphoric acid salts, glycerophosphoric acid salts, hydrogen phosphoric acid salts, dihydrogen phosphoric acid salts, and sodium nitrate are preferably employed, dihydrogen phosphoric acid salts, glycerophosphoric acid salts and metaphosphoric acid salts are more preferably employed and glycerophosphoric acid salts and metaphosphoric acid salts are still more preferably employed.

[0081] In the above-mentioned salts, the metal moiety is preferably selected from sodium, potassium, calcium, magnesium, and aluminum, and more preferably, from sodium, potassium, calcium and magnesium.

[0082] Especially, the metaphosphoric acid salts, for example, sodium metaphosphate and potassium metaphosphate are advantageously employed.

[0083] There is no limitation to the content of the phosphoric acid salts and nitric acid salts in the recording sheet. Usually, in view of gloss and compatibility with the coating liquid, the salts are preferably selected from those having a solubility of 2 g/liter in water at a temperature of 20°C. Also, the salts are preferably contained in a content of 0.1 to 5 g/m², more preferably 0.2 to 2.5 g/m², in the recording material. When the salt content is too low, the light fastness-enhancing effect may be insufficient, and when the salt content is too high, the resultant coating liquid may exhibit an insufficient film-forming property and the resultant ink receiving layer may exhibit an unsatisfactory gloss.

[0084] When a mat ink jet recording material having a low gloss is comprised of the phosphoric acid salts and/or the nitric acid salts, the resultant light fastness-enhancing effect is not very high. The reasons for this phenomenon have not yet been made clear. It is assumed that since the ink receiving layer of the mat ink jet recording material is usually formed from pigment particles having a particle size of several μm and a binder, the phosphoric acid salts and the nitric acid salts added to the ink receiving layer are easily absorbed in the gaps between the pigment particles, and thus cannot exhibit the light fastness-enhancing effect. However, in the present invention, to provide an ink jet recording material capable of recording ink images having an excellent color density and sharpness thereon, the gloss of the recording material surface is enhanced.

[0085] In the recording material of the present invention, the ink receiving layer is formed from a composition which causes a diffused reflection of light on the ink receiving layer to be difficult, to enhance the gloss of the ink receiving layer surface. In this case, the resultant ink receiving layer exhibits low light fastness and use-life, for unknown reasons. When the phosphoric acid salts or nitric acid salts are contained in the ink receiving layer of the ink jet recording material having a high gloss, the salts exhibit a high light fastness-enhancing effect on the ink images recorded on the ink receiving layer.

[0086] The ink receiving layer may be formed only of the above-mentioned layer. To enhance the ink-absorbing property, the ink receiving layer can be multi-layered. In the multi-layered ink receiving layer, at least one special layer, preferably an upper layer, preferably has the above-mentioned structure. The special layer may be formed from the above-mentioned polymeric materials (resins). Also, the special layer may be formed from a pigment having the above-mentioned specific particle size or an other pigment having another particle size and a binder resin, and optionally a cationic polymeric material (resin).

[0087] There is no limitation to the amount of the ink receiving layer. Usually, the ink receiving layer is preferably formed in an amount of 3 to 60 g/m², more preferably 10 to 50 g/m², in a single layer structure. When the ink receiving layer is formed in a multi-layered structure, the upper layer is preferably in an amount of 3 to 30 g/m², more preferably 5 to 20 g/m² and the lower layer is preferably in an amount of 1 to 50 g/m², more preferably 5 to 40 g/m².

[0088] In the ink jet recording material of the present invention, the support material is not limited to a specific form of material. The support material may be transparent or may be opaque. The support material is formed from at least one member selected from various paper sheets, for example, woodfree paper sheets, art paper sheets, coated paper sheets, cast-coated paper sheets, foil-laminated paper sheets, kraft paper sheets, polyethylene-laminated paper sheets, impregnated paper sheets, metallized paper sheets and water-soluble paper sheets; cellulose films; plastic films, for example, polyethylene, propylene, soft polyvinyl chloride, hard polyvinyl chloride, and polyester films; metal foils and synthetic paper sheets.

[0089] The ink receiving layer is formed on the support material by using conventional coating means, for example, die coater, blade coater, air knife coater, roll coater, bar coater, gravure coater, rod blade coater, lip coater and curtain coater.

[0090] In the present invention, the ink receiving layer having a high gloss can be formed in such a manner that at least one layer, preferably an upper layer to which the ink images are recorded, is formed, in the form of a film, on a casting surface of a casting base; the surface of the support material (or, when the ink receiving layer is in a multi-layered structure, a surface of a layer formed on the support material) is brought into contact with and adhered to the layer surface on the casting surface under pressure, to transfer the casted layer from the casting surface to the support material; and the resultant composite consisting of the support material and the transferred layer is separated from the casting surface.

[0091] The casting base having the casting surface is preferably selected from sheet materials having a high surface smoothness and a high flexibility, for example, cellulose films, and plastic films, for example polyethylene polypropylene, soft polyvinyl chloride, hard polyvinyl chloride, and polyester films; paper sheets, for example, polyethylene-laminated paper sheets, glassine paper sheets, impregnated paper sheets, and metallized paper sheets; metal foils, and synthetic paper sheets. Also, the casting base may be selected from drums and plates consisting of an inorganic glass, metal or plastics, having a high surface smoothness. Preferably, plastic films (for example, polyethylene, polypropylene and polyester films) and metal drums having a high smoothness surface are preferably employed as a casting

base, because these casting bases enable the casted layer to be easily formed and the resultant casted layer can be easily separated from the casting surface.

[0092] For the purpose of imparting a high smoothness to the ink receiving layer, the casting surface preferably has a high smoothness. In this case, the casting surface preferably has a surface roughness Ra of 0.5 μm or less, more preferably 0.05 μm or less, determined in accordance with Japanese Industrial Standard (JIS) B 0601.

[0093] The ink receiving layer may have a semi-gloss surface or mat surface which can be formed by controlling the surface roughness Ra of the casting surface.

[0094] The casting surface may be a non-surface treated surface. However, to control the adhesion between the casted layer for the ink receiving layer and the support material (or other layer of the ink receiving layer when the ink receiving layer is in a multi-layered structure) to a level lower than the adhesion between the casting surface and the cast layer, the casting surface of the casting base is preferably coated with a releasing material, for example, a silicone or fluorine-containing compound. As long as the cast layer formed on the casting surface can be adhered to the support material (or a coating layer coated on the support material when the ink receiving layer has a multi-layered structure), there is no limitation to the adhesion method for the cast layer with the support material (or the coating layer on the support material). For example, the adhesion can be effected by superposing a support material on a cast layer formed on the casting surface of a casting base consisting of a plastic film, and pressing the superposed composite by passing it through a pair of pressing rollers. When the casting base is a casting drum having a casting peripheral surface, the superposed composite is pressed between the casting drum and a pressing roller. Also, when the superposed composite must be heated, the press rollers or the casting drum may be utilized as a heater. The adhesion can be effected only by heating at a temperature of preferably 30 to 100°C and by pressing under a pressure of preferably 49 - 1471 N/cm (5 to 150 kg/cm). Preferably, during the adhesion procedure, the water content of the upper layer and/or the lower layer of the ink receiving layer is controlled to 50 to 350% based on the total bone-dry weight of the ink receiving layer, by blowing water vapor or by applying water to the layer or layers, in other words, water is imparted in an amount of 50 to 350 parts by weight per 100 parts by bone-dry weight of the ink receiving layer to the upper layer and/or the lower layer; and then the water content-controlled superposed composite is pressed. The support material may have an intermediate layer (formed from an adhesive or pressure-sensitive adhesive and having an adhesive property or sticking property) and may be adhered to the cast layer through the intermediate layer. More preferably, the intermediate layer has an ink-absorbing property, and thus can be utilized as a portion of the ink receiving layer. In this case, the ink-absorbing intermediate layer is formed on the support material, and then while in wetted condition the intermediate layer is adhered to the casted layer and dried.

[0095] The ink usable for the ink jet recording material of the present invention must comprise, as indispensable components, a coloring material for forming colored images and a liquid medium for dissolving or dispersing the coloring material therein. The ink optionally contains at least one additive selected from, for example, dispersing agents, viscosity modifiers, specific resistivity modifiers, pH modifiers, mildewproofing agents, stabilizers for dissolution or dispersion of the coloring materials, and surfactants other than the above-mentioned agents.

[0096] The coloring material usable for the ink may be selected from direct dyes, acid dyes, basic dyes, reactive dyes, edible coloring matters, disperse dyes, oil dyes and coloring pigments. These coloring materials can be selected from conventional coloring materials without limitation. The content of the coloring material in the ink is designed in response to the type of the liquid medium and the requirements for the ink. In the ink usable for the ink jet recording material of the present invention, the coloring material is contained in an amount similar to that of the conventional inks, namely in a content of 0.1 to 20% by weight.

[0097] The liquid medium of the ink usable for the ink jet recording material of the present invention comprises at least one member selected from water and water-soluble organic solvents, for example, alkyl alcohols having 1 to 4 carbon atoms, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol; ketones and ketonealcohols, polyalkylene glycols, alkylene glycols in which the alkylene group has 2 to 6 carbon atoms, and lower alkyl (C_2 to C_5) ethers of polyhydric alcohols.

EXAMPLES

[0098] The present invention will be further explained by the following examples which are not intended to restrict the scope of the present invention in any way.

Example I-1

[0099] An ink jet recording paper sheet was prepared by coating a surface of a trade-available PPC paper sheet with a 10% by weight aqueous solution of arbutin (chemical reagent grade, made by TOKYO KASEIKOGYO K.K.) by using a bar coater and drying. The dry content of arbutin in the resultant recording sheet was 0.3 g/m².

Example I-2

[0100] A trade available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO., LTD.) was coated on a surface thereof with a coating liquid having the composition shown below and a solid content of 7% by using a die coater and dried to form an ink receiving layer on the paper sheet. The dry weight of the resultant ink receiving layer was 20 g/m².

Coating liquid composition (total solid content: 7% by weight)	
Component	Part by dry weight
Amorphous silica (trademark: FINESIL X-45, made by TOKUYAMA K.K., average agglomerated particle size: 4.5 μ m)	100
Silyl-modified polyvinyl alcohol (trademark: PVA-R-1130, made by K.K. KURARAY)	35
Cationic resin (Polydiallyldimethyl ammonium chloride, (trademark: PAS-H-10L, made by NITTO BOSEKI K.K.))	15
Arbutin (Chemical reagent grade, made by TOKYO KASEIKOGYO K.K.)	5

Example I-3

[0101] An ink jet recording paper sheet was prepared by the same procedures as in Example I-1 except that the coating liquid for the ink receiving layer was prepared by the following procedures.

Coating liquid composition (total solid content: 7% by weight)	
Component	Part by dry weight
Silica sol A	100
Polyvinyl alcohol (trademark: PVA-135H, made by K.K. KURARAY)	35
Arbutin (Chemical reagent grade, made by TOKYO KASEIKOGYO K.K.)	5

Preparation of silica sol I-A

[0102] A synthetic amorphous silica (trademark: NIPSIL HD-2, made by NIPPON SILICA KOGYO K.K.) having a primary particle size of 11 nm and an average agglomerated particle size of 3 μ m was pulverized and dispersed by a sand grinder and then further pulverized and dispersed by a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average agglomerated particle size reached 70 nm, to prepare an aqueous dispersion containing the amorphous silica in a dry content of 8% by weight.

[0103] The aqueous amorphous silica dispersion in an amount of 100 parts by solid weight was mixed with 15 parts by solid weight of a cationic resin comprising of polydiallyldimethyl ammonium chloride (trademark: PAS-H-10L, made by NITTO BOSEKI K.K.) to increase the viscosity of the dispersion and then to coagulate the dispersion. The resultant coagulation was pulverized and dispersed by using a sand grinder and further pulverized and dispersed by using a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average particle size reached 490 nm. The resultant aqueous silica sol I-A had a solid content of 9% by dry weight.

Example I-4

[0104] An ink jet recording paper sheet was prepared by the same procedures as in Example I-3 with the following exceptions.

[0105] In the formation of the ink receiving layer, the coating liquid contained no arbutin. Then the resultant ink

receiving layer was coated with a 10% by weight aqueous solution of arbutin (chemical reagent grade, made by TOKYO KASEIGOKYO K.K.) by using a bar coater and dried, to cause the arbutin to be contained in a dry amount of 1.0 g/m² in the ink jet recording sheet.

5 Example I-5

[0106] An ink jet recording sheet was produced by the same procedures as in Example I-3, except that arbutin was replaced by hydroquinone (chemical reagent grade, made by KANTO KAGAKU K.K.).

10 Example I-6

[0107] An ink jet recording sheet was produced by the same procedures as in Example I-4, with the following exceptions.

15 [0108] The same coating liquid for the ink receiving layer as in Example I-4 was coated on a surface of a casting base consisting of a PET film (trademark: LUMILER T, made by TORAY INDUSTRIES INC.) having a thickness of 50 µm Ra of 0.02 µm and used in place of the coated paper sheet (trademark: OK COAT, made by OJI PAPER CO.) having a basis weight of 127.9 g/m², to form an ink receiving layer.

20 [0109] The same coating liquid for the ink receiving layer as mentioned above was coated in a solid amount of 10 g/m² on a surface of a trade available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO.) having a basis weight of 127.9 g/m², the coated paper sheet was superposed on the coating layer on the PET film surface in a manner such that the coating layer on the paper sheet came into contact with the coating layer on the PET film, the superposed composite was dried and the PET film was peeled off from the resultant ink jet recording sheet.

Example I-7

25 [0110] An ink jet recording paper sheet was produced by the same procedures as in Example I-3, with the following exceptions.

30 [0111] In the preparation of the coating liquid for the ink receiving layer, the amorphous silica was replaced by polyvinyl alcohol (trademark: PVA 420, made by K.K. KURARAY) and arbutin was replaced by hydroquinone monobenzylether (chemical reagent grade, made by TOKYO KASEIKOGYO K.K.). Also, the coated paper sheet for the support material was replaced by a resin-coated paper sheet which will be explained below.

Preparation of resin-coated paper sheet for support material

35 [0112] An aqueous pulp slurry having a solid content of 0.5% by weight was prepared from a mixture of a soft wood bleached kraft pulp (NBKP) pulped to a Canadian Standard Freeness (CSF) of 300 ml determined in accordance with Japanese Industrial standard P8121 with a hard wood bleached kraft pulp (LBKP) pulped to a CSF of 350 ml in a mixing weight ratio of 2:8. The pulp slurry was added with 2.0% by weight of a cationic starch, 0.4% by weight of alkylketene dimer, 0.1% by weight of an anionic polyacrylamide resin and 0.7% by weight of a polyamidepolyamine epichlorohydrin resin based on the bone-dried total weight of the pulps in the pulp slurry, and the mixed slurry was fully agitated to uniformly disperse the solid components in the aqueous slurry.

40 [0113] The aqueous pulp slurry having the above-mentioned composition was subjected to a paper-forming procedure using a Fourdrinier paper machine, a dryer, a size-press, and a machine calender, to produce a paper sheet having a base weight of 128 g/m² and a bulk density of 1.0 g/cm³. In the sizing procedure, a sizing liquid, produced by heat-dissolving a mixture of a carboxyl-modified polyvinyl alcohol with sodium chloride in a mixing weight ratio of 2:1 in water, and having a solid concentration of 5% by weight, was applied in an amount of 25 ml to each surface of the paper sheet.

45 [0114] A corona discharge treatment was applied to both the surfaces of the paper sheet, then a polyolefin resin composition (1) having the composition shown below was coated in an amount of 25 g/m² on the felt side surface of the paper sheet, and a polyolefin resin composition (2) having the composition shown below was coated in an amount of 25 g/m² on the wire side surface of the paper sheet, through T-dies of a melt extruder at a melt temperature of 320°C, and the melt-coated layers were cool-solidified by a mirror-finished peripheral surfaces of cooling rolls, to prepare a support sheet.

Polyolefin resin composition (1)	
Component	Part by dry weight
Long linear low density polyethylene resin (density: 0.926 g/cm ³ , melt index: 20g/10 minutes)	35
Low density polyethylene resin (density: 0.919 g/cm ³ , melt index: 2g/10 minutes)	50
Anatase type titanium dioxide (trademark: A-220, made by ISHIHARA SANGYO K.K.)	15
Zinc Stearate	0.1
Anti-oxidant (trademark: IRGANOX 1010, made by CIBA-GEIGY)	0.03
Ultramarine (BLuish ULTRAMARINE No. 2000, made by DAIICHI KASEI K.K.)	0.09
Fluorescent brightening agent (trademark: UNITEX OB, made by CIBA-GEIGY)	0.3
Polyolefin resin composition (2)	
Component	Part by dry weight
High density polyethylene resin (density: 0.954 g/cm ³ , melt index: 20g/10 minutes)	65
Low density polyethylene resin (density: 0.924 g/cm ³ , melt index: 4g/10 minutes)	35
Note: In the polyolefin resin composition (1), the anti-oxidant was employed to prevent the oxidation of the polyethylene resins during the melt-extrusion procedure and the ultramarine and the fluorescent brightening agent were employed to impart a bluing effect and apparent whitening effect to the resin composition and to improve the naked eye appearance of the resultant coating layer.	

Comparative Example I-1

[0115] An ink jet recording sheet was produced by the same procedures as in Example I-1, except that no arbutin was employed.

Comparative Example I-2

[0116] An ink jet recording sheet was produced by the same procedures as in Example I-2, except that a hindered amine photostabilizing agent (trademark: CHINUBIN 144, made by CIBA-GEIGY), was employed in place of arbutin.

Comparative Example I-3

[0117] An ink jet recording sheet was produced by the same procedures as in Example I-2, except that a benzotriazole ultraviolet ray absorber (trademark: JF-77, made by JOHOKU KAGAKU K.K.) was employed in place of arbutin.

TESTS

[0118] The ink jet recording sheets of the Examples I-1 to I-7 and Comparative Example I-1 to I-3 were subjected to the tests for evaluating the color density, light fastness and water resistance of ink images recorded thereon.

[0119] The tests were carried out by the following methods.

[0120] In the tests, the recording sheet were printed by using an ink jet printer (trademark: PM-750C, made by EPSON).

(1) Color density of recorded images

[0121] A solid print was formed with a black-colored ink on each recording sheet, and the color density of the solid print was measured three times by the Macbeth reflection color density tester (model: RD-920, made by Macbeth). An average of the measured color density data was calculated.

(2) Light fastness of recorded images

[0122] On each recording sheet, ISO-400 images ("High accuracy color digital standard image data, ISO/JIS-SCID", page 13, name of image: Fruit basket, and page 14, name of image: Candle, published by ZAIDANHOGIN NIPPON KIKAKU KYOKAI) in a gloss paper mode, and the printed images was subjected to a continuous fading treatment using a xenon lamp-using FADE-OMETER (model: CI35F, made by ATLAS ELECTRIC DEVICES CO.) at 63°C at 50% RH for 50 hours. The tested images were compared with the original images and evaluated as follows.

Class	Tested images
4	Substantially no color-fading is found.
3	Slight color-fading is found. Practically usable.
2	Color is faded to such an extent that color balance is lost. Practically unusable.
1	Color is greatly faded and color balance is significantly lost.

(3) Water resistant of recorded images

[0123] After the recorded sheet was left to stand for 24 hours in the ambient atmosphere, a drop of water was placed on the images, and one minute after the placing, the water drop was removed by wiping. The water-wetted portion of the images was observed by the naked eye to evaluate the water resistance of the images as follows.

Class	Water resistance
3	Substantially no ink in the images was removed.
2	A portion of the ink in the images was removed.
1	The ink images were completely removed.

[0124] The test results are shown in Table 1.

Table 1

Example No.	Item	Recorded ink images		
		color density	Light fastness	Water resistance
Example	I-1	1.30	3	2
	I-2	1.75	4	3
	I-3	2.45	4	3
	I-4	2.40	4	3
	I-5	2.45	3	3
	I-6	2.55	4	3
	I-7	2.50	3	2
Comparative Example	I-1	1.25	1	2
	I-2	1.72	2	3
	I-3	1.70	2	3

[0125] Table 1 clearly shows that the ink jet recording sheet of Examples I-1 to I-7 containing hydroquinone or hydroquinone derivatives enabled the recorded ink images to exhibit a high light fastness.

[0126] Particularly, in Examples I-2 to I-4 in which, as a hydroquinone derivative, arbutin was contained in an amount of 0.6 g/m² in the recording sheets, the recorded ink images exhibited a very high light fastness.

[0127] In Examples I-2 to I-6 in which a pigment and/or a cationic resin were employed in addition to the hydroquinone derivatives, the resultant ink images exhibited a high color density and a high water resistance. Especially, in Examples I-3 to I-6 wherein fine silica particles having a particle size of 1 μ m or less were employed as an ink absorbing material, the resultant ink images exhibited an excellent color density and a high sharpness.

[0128] In comparative Example I-1 wherein no light fastness-enhancing agent was employed, the resultant ink images exhibited a very poor light fastness.

[0129] In comparative Examples I-2 and I-3 wherein a light fastness-enhancing agent other than that of the present invention was employed, the resultant ink images exhibited an unsatisfactory light fastness.

Example II-1

[0130] An ink jet recording paper sheet was produced by coating a surface of a trade-available PPC paper sheet (recycled PPC paper sheet having a basis weight of 64 g/m², made by FUJI XEROX K.K.) with a 5% by weight aqueous dispersion liquid of pyrocatechol-3-carboxylic acid (chemical reagent grade) by using a bar coater, and dried. The dry amount of pyrocatechol-3-carboxylic acid in the resultant recording paper sheet was 0.3 g/m².

Example II-2

[0131] An ink jet recording paper sheet was produced by coating a surface of a trade-available PPC paper sheet (recycled PPC paper sheet having a basis weight of 64 g/m², made by FUJI XEROX K.K.) with a 5% by weight aqueous dispersion liquid of sodium pyrocatechol-acetate (chemical reagent grade) by using a bar coater, and dried. The dry amount of sodium pyrocatechol acetate in the resultant recording paper sheet was 0.3 g/m².

Example II-3

[0132] An ink jet recording paper sheet was produced by coating a surface of a trade-available PPC paper sheet (recycled PPC paper sheet having a basis weight of 64 g/m², made by FUJI XEROX K.K.) with a 5% by weight aqueous dispersion liquid of pyrocatechol-3,6-dicarboxylic acid (chemical reagent grade) by using a bar coater, and dried. The dry amount of pyrocatechol-3,6-dicarboxylic acid in the resultant recording paper sheet was 0.3 g/m².

Example II-4

[0133] An ink jet recording paper sheet was produced by coating a surface of a trade-available PPC paper sheet (recycled PPC paper sheet having a basis weight of 64 g/m², made by FUJI XEROX K.K.) with a 5% by weight aqueous

dispersion liquid of disodium pyrocatechol-3,5-disulfonate (Tailon, chemical reagent grade) by using a bar coater, and dried. The dry amount of disodium pyrocatechol-3,5-disulfonate in the resultant recording paper sheet was 0.3 g/m².

Example II-5

[0134] An ink jet recording paper sheet was produced by coating a trade-available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO., LTD.) having a basis weight of 127.9 g/m² with an aqueous coating liquid for an ink receiving layer having the composition as shown below, by using a bar coater, to form an ink receiving layer having a dry weight of 20 g/m².

Coating liquid composition for ink receiving layer	
Component	Part by dry weight
Amorphous silica having an average secondary particle size of 4.5 µm and an average primary particle size of 15 nm (trademark: FINESIL X-45, made by TOKUYAMA K.K.)	100
Silyl-modified polyvinyl alcohol (trademark: PVA-R-1130, made by K.K. KURARAY)	35
Cationic resin (Polydiallyldimethyl ammonium chloride, (trademark: PAS-H-10L, made by NITTO BOSEKI K.K.)	15
Disodium pyrocatechol-3,5-disulfonate (Tailon, chemical reagent grade)	5

[0135] The aqueous coating liquid had a solid content of 14% by weight.

Example II-6

[0136] An ink jet recording paper sheet was prepared in the same procedures as in Example II-5, except that the aqueous coating liquid for the ink receiving layer was prepared in the following composition.

Coating liquid composition	
Component	Part by dry weight
Silica sol II-A	100
Polyvinyl alcohol (trademark: PVA-135H, made by K.K. KURARAY)	35
Disodium pyrocatechol-3,5-disulfonate (chemical reagent grade, Tailon)	5

[0137] The aqueous coating liquid had a solid content of 10% by weight.

Preparation of silica sol II-A

[0138] A synthetic amorphous silica (trademark: NIPSIL HD-2, made by NIPPON SILICA KOGYO K.K.) having a primary particle size of 11 nm and an average agglomerated particle size of 3 µm was pulverized and dispersed by a sand grinder and then further pulverized and dispersed by a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average agglomerated particle size reached 70 nm, to prepare an aqueous dispersion containing the amorphous silica in a dry content of 9% by weight.

[0139] The aqueous amorphous silica dispersion in an amount of 100 parts by solid weight was mixed with 15 parts by solid weight of a cationic resin comprising of polydiallyldimethyl ammonium chloride (trademark: PAS-H-10L, made by NITTO BOSEKI KOGYO K.K.) to increase the viscosity of the dispersion and then to coagulate the dispersion. The resultant coagulation was pulverized and dispersed by using a sand grinder and further pulverized and dispersed by using a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average particle size reached 470 nm. The resultant aqueous silica sol

II-A had a solid content of 10% by dry weight.

Example II-7

5 [0140] An ink jet recording paper sheet was prepared in the same procedures as in Example II-6 with the following exceptions.

[0141] In the coating liquid for the ink receiving layer, no disodium pyrocatechol-3,5-disulfonate (Tailon) was contained.

10 [0142] The aqueous coating liquid was used to form a coating layer on the coated paper sheet. Then the coating layer was coated with an aqueous solution of 6% by weight of disodium pyrocatechol-3,5-disulfonate by using a bar coater and dried, to cause the disodium pyrocatechol-3,5-disulfonate to be contained in a dry amount of 0.6 g/m² to form an ink receiving layer.

Example II-8

15 [0143] An ink jet recording sheet was produced by the same procedures as in Example II-6, with the following exceptions.

[0144] The same coating liquid for the ink receiving layer as in Example I-4 except that no disodium pyrocatechol-3,5-disulfonate was contained, was coated on a surface of a casting base consisting of a PET film (trademark: LUMILER T, made by TORAY INDUSTRIES INC.) having a thickness of 50 µm and an Ra of 0.02 µm, and an aqueous solution of 6% by weight of disodium pyrocatechol-3,5-disulfonate was coated on the resultant coating layer by using a bar coater and dried, to cause the disodium pyrocatechol-3,5-disulfonate to be contained in the coating layer and to form an upper layer of an ink receiving layer on the casting base.

25 [0145] The same coating liquid containing no disodium pyrocatechol-3,5-disulfonate for the ink receiving layer as mentioned above was coated in a solid amount of 5 g/m² on a surface of a trade available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO.) having a basis weight of 127.9 g/m² by using a bar coater, to form a lower layer of the ink receiving layer, the coated paper sheet was superposed on the coating layer on the PET film surface in a manner such that the coating layer on the paper sheet came into contact with the coating layer on the PET film, the superposed composite was dried and the PET film was peeled off from the resultant ink jet recording sheet.

Comparative Example II-1

[0146] A PPC paper sheet (recycled PPC paper sheet having a basis weight of 64 g/m², made by FUJI XEROX) was used as an ink jet recording paper sheet.

Comparative Example II-2

40 [0147] An ink jet recording paper sheet was prepared in the same procedures as in Example II-1, except that disodium pyrocatechol-3,5-disulfonate was replaced by a benzotriazole ultraviolet ray absorber (trademark: JF-77, made by JOHOKU KAGAKU K.K.).

Comparative Example II-3

45 [0148] An ink jet recording paper sheet was prepared in the same procedures as in Example II-1, except that disodium pyrocatechol-3,5-disulfonate was replaced by resorcinol (chemical reagent grade, made by KANTO KAGAKU K.K.).

Comparative Example II-4

50 [0149] An ink jet recording paper sheet was prepared in the same procedures as in Example II-1, except that disodium pyrocatechol-3,5-disulfonate was replaced by a hindered amine (trademark: LA-57, made by ASAHI DENKAKO-GYO K.K.).

Comparative Example II-5

55 [0150] An ink jet recording paper sheet was prepared in the same procedures as in Example II-1, except that disodium pyrocatechol-3,5-disulfonate was replaced by phosphotungstic acid (chemical reagent grade, made by KANTO KAGAKU K.K.).

TESTS

[0151] The ink jet recording sheets of the Examples II-1 to II-8 and Comparative Examples II-1 to II-5 were subjected to the tests for evaluating the color density and light fastness of ink images recorded thereon and the gloss.

[0152] The tests were carried out by the following methods. In the tests, the recording sheet were printed by using an ink jet printer (trademark: PM-750C, made by EPSON).

(1) Color density of recorded images

[0153] A solid print was formed with a black-colored ink on each recording sheet, and the color density of the solid print was measured three times by the Macbeth reflection color density tester (model: RD-920, made by Macbeth). An average of the measured color density data was calculated.

(2) Light fastness of recorded images

[0154] On each recording sheet, ISO-400 images ("High accuracy color digital standard image data, ISO/JIS-SCID", page 13, name of image: Fruit basket, and page 14, name of image: Candle, published by ZAIDANHOGIN NIPPON KIKAKU KYOKAI) in a gloss paper mode, and the printed images was subjected to a continuous fading treatment using a xenon lamp-using FADE-OMETER (model: CI35F, made by ATLAS ELECTRIC DEVICES CO.) at 63°C at 50% RH for 50 hours. The tested images were compared with the original images and evaluated as follows.

Class	Tested images
4	Substantially no color-fading is found.
3	Slight color-fading is found. Practically usable.
2	Color is faded to such an extent that color balance is lost. Practically unusable.
1	Color is greatly faded and color balance is significantly lost.

(3) Gloss

[0155] A 75 degree mirror-finished surface gloss in accordance with Japanese Industrial Standard (JIS) Z 8741 of each recording sheet surface was measured by a glossmeter made by NIPPON DENSHOKUKOGYO K.K.

[0156] The test results are shown in Table 2.

Table 2

Example No.	Item	Recorded ink images		75 degree gloss
		color density	Light fastness	
Example	II-1	1.30	3	10>
	II-2	1.27	3	10>
	II-3	1.29	3	10>
	II-4	1.31	4	10>
	II-5	1.76	4	10>
	II-6	2.42	4	50
	II-7	2.40	4	46
	II-8	2.51	4	68
Comparative Example	II-1	1.28	1	10>
	II-2	1.25	2	10>
	II-3	1.30	2	10>
	II-4	1.24	2	10>
	II-5	1.26	2	10>

[0157] Table 2 shows that the ink images recorded on the recording sheets containing pyrocatechol derivatives exhibited a high light fastness. Especially, the pyrocatechol-3,5-disulfonic acid salt caused the recorded ink images to exhibit an excellent light fastness.

Example III-1

[0158] An ink jet recording paper sheet was prepared by coating a surface of a trade-available PPC paper sheet (woodfree copying plane paper sheet) with a 10% by weight aqueous solution of a light fastness-enhancing agent consisting of sodium *p*-hydroxybenzenesulfonate (chemical reagent grade, made by KANTO KAGAKU K.K.) by using a bar coater and drying. The dry content of the light fastness-enhancing agent in the resultant recording sheet was 0.3 g/m².

Example III-2

[0159] A trade available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO., LTD.) having a basis weight of 127.9 g/m² was coated on a surface thereof with a coating liquid having the composition shown below and a solid content of 7% by using a die coater and dried to form an ink receiving layer on the paper sheet. The dry weight of the resultant ink receiving layer was 20 g/m².

Coating liquid composition (total solid content: 7% by weight)		
Component		Part by dry weight
Amorphous silica (trademark: FINESIL X-45, made by TOKUYAMA K.K., average agglomerated particle size: 4.5 μm)		100
Silyl-modified polyvinyl alcohol (trademark: PVA-R-1130, made by K.K. KURARAY)		35
Cationic resin (Polydiallyldimethyl ammonium chloride, (trademark: PAS-H-10L, made by NITTO BOSEKI K.K.)		15
Sodium <i>p</i> -hydroxybenzenesulfonate (Chemical reagent grade, made by KANTO KAGAKU K.K.)		5

Example III-3

[0160] An ink jet recording paper sheet was prepared by the same procedures as in Example III-2 except that the coating liquid for the ink receiving layer was prepared by the following procedures.

Coating liquid composition (total solid content: 7% by weight)	
Component	Part by dry weight
Silica sol III-A	100
Polyvinyl alcohol (trademark: PVA-135H, made by K.K. KURARAY)	35
Sodium p-hydroxybenzenesulfonate (Chemical reagent grade, made by KANTO KAGAKU K.K.)	5

Preparation of silica sol III-A

[0161] A synthetic amorphous silica (trademark: NIPSIL HD-2, made by NIPPON SILICA KOGYO K.K.) having a primary particle size of 11 nm and an average agglomerated particle size of 3 μm was pulverized and dispersed by a sand grinder and then further pulverized and dispersed by a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average agglomerated particle size reached 70 nm, to prepare an aqueous dispersion containing the amorphous silica in a dry content of 8% by weight.

[0162] The aqueous amorphous silica dispersion in an amount of 100 parts by solid weight was mixed with 15 parts by solid weight of a cationic resin comprising of polydiallyldimethyl ammonium chloride (trademark: PAS-H-10L, made by NITTO BOSEKI KOGYO K.K.) to increase the viscosity of the dispersion and then to coagulate the dispersion. The resultant coagulation was pulverized and dispersed by using a sand grinder and further pulverized and dispersed by using a pressure type homogenizer, and the pulverizing and dispersing procedures using the sand grinder and the pressure type homogenizer were repeated until the average particle size reached 490 nm. The resultant aqueous silica sol III-A had a solid content of 9% by dry weight.

Example III-4

[0163] An ink jet recording paper sheet was prepared by the same procedures as in Example I-3 with the following exceptions.

[0164] In the formation of the ink receiving layer, the coating liquid contained no sodium p-hydroxybenzenesulfonate. Then, the resultant ink receiving layer was coated with a 10% by weight aqueous solution of sodium p-hydroxybenzenesulfonate (chemical reagent grade, made by KANTO KAGAKU K.K.) by using a bar coater and dried, to cause the sodium p-hydroxybenzenesulfonate to be contained in a dry amount of 1.0 g/m² in the ink jet recording sheet.

Example III-5

[0165] An ink jet recording sheet was produced by the same procedures as in Example III-3, except that sodium p-hydroxybenzenesulfonate was replaced by disodium 2-naphthol-3,6-disulfonate (chemical reagent grade, made by KANTO KAGAKU K.K. and referred to "R acid disodium salt").

Example III-6

[0166] An ink jet recording paper sheet was produced by the following procedures.

[0167] An aqueous coating liquid containing 100 parts by weight of the silica sol III-A and 35 parts by weight of polyvinyl alcohol (trademark: PVA-135H, made by KURARAY K.K.) and having a solid content of 7% by weight was coated, by using a bar coater, on a surface of a casting base consisting of a PET film (trademark: LUMILER T, made by TORAY INDUSTRIES INC.) having a thickness of 50 μm , and dried, to form a coating layer having a dry weight of 20 g/m². The coating layer was coated with a 10% by weight aqueous solution of sodium p-hydroxybenzenesulfonate by using a bar coater and dried, to cause the sodium p-hydroxybenzenesulfonate to be contained in a dry weight of 1.0 g/m² in the coating layer and to form an upper layer of an ink receiving layer.

[0168] The same coating liquid as mentioned above was coated in a solid amount of 10 g/m² on a surface of a trade available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO.) having a basis weight of 127.9 g/m², the coated paper sheet was superposed on the coating layer on the PET film surface in a manner such that the coating layer on the paper sheet came into contact with the coating layer on the PET film, the superposed composite was dried and the PET film was peeled off from the resultant ink jet recording sheet.

Example III-7

[0169] An ink jet recording paper sheet was prepared by the following procedures.

[0170] A resin-coated paper sheet for a support sheet was prepared in the following manner.

[0171] An aqueous pulp slurry having a solid content of 0.5% by weight was prepared from a mixture of a soft wood bleached kraft pulp (NBKP) pulped to a Canadian Standard Freeness (CSF) of 300 ml determined in accordance with Japanese Industrial Standard P8121 with a hard wood bleached kraft pulp (LBKP) pulped to a CSF of 350 ml in a mixing weight ratio of 2:8. The pulp slurry was added with 2.0% by weight of a cationic starch, 0.4% by weight of alkylketene dimer, 0.1% by weight of anionic polyacrylamide resin and 0.7% by weight of a polyamidepolyamine epichlorohydrin resin based on the bone-dried total weight of the pulps in the pulp slurry, and the mixed slurry was fully agitated to uniformly disperse the solid components in the aqueous slurry.

[0172] The aqueous pulp slurry having the above-mentioned composition was subjected to a paper-forming procedure using a Fourdrinier paper machine, a dryer, a size-press, and a machine calender, to produce a paper sheet having a base weight of 180 g/m² and a bulk density of 1.0 g/cm³. In the sizing procedure, a sizing liquid prepared by heat-dissolving a mixture of a carboxyl-modified polyvinyl alcohol with sodium chloride in a mixing weight ratio of 2:1 in water, and having a solid concentration of 5% by weight was applied in an amount of 25 ml to each surface of the paper sheet.

[0173] A corona discharge treatment was applied to both the surfaces of the paper sheet, then a polyolefin resin composition (1) having the composition shown below was coated in an amount of 25 g/m² on the felt side surface of the paper sheet, and a polyolefin resin composition (2) having the composition shown below was coated in an amount of 25 g/m² on the wire side surface of the paper sheet, through T-dies of a melt extruder at a melt temperature of 320°C, and the melt-coated layers were cool-solidified by a mirror-finished peripheral surfaces of cooling rolls, to prepare a support sheet.

Polyolefin resin composition (1)		
	Component	Part by dry weight
5	Long linear low density polyethylene resin (density: 0.926 g/cm ³ , melt index: 20g/10 minutes)	35
10	Low density polyethylene resin (density: 0.919 g/cm ³ , melt index: 2g/10 minutes)	50
	Anatase type titanium dioxide (trademark: A-220, made by ISHIHARA SANGYO K.K.)	15
15	Zinc Stearate	0.1
	Anti-oxidant (trademark: IRGANOX 1010, made by CIBA-GEIGY)	0.03
	Ultramarine (BLUISH ULTRAMARINE No. 2000, made by DAIICHI KASEI K.K.)	0.09
20	Fluorescent brightening agent (trademark: UNITEX OB, made by CIBA-GEIGY)	0.3
Polyolefin resin composition (2)		
	Component	Part by dry weight
25	High density polyethylene resin (density: 0.954 g/cm ³ , melt index: 20g/10 minutes)	65
30	Low density polyethylene resin (density: 0.924 g/cm ³ , melt index: 4g/10 minutes)	35
35	Note: In the polyolefin resin composition (1), the anti-oxidant was employed to prevent the oxidation of the polyethylene resins during the melt-extrusion procedure and the ultramarine and the fluorescent brightening agent were employed to impart a bluing effect and apparent whitening effect to the resin composition and to improve the naked eye appearance of the resultant coating layer.	

[0174] A coating liquid having the composition shown below was prepared.

Coating liquid composition for ink receiving layer		
	Component	Part by dry weight
40	Polyvinyl alcohol (trademark: PVA420, made by K.K. KURARAY)	100
45	Silyl-modified polyvinyl alcohol (trademark: PVA-R-1130, made by K.K. KURARAY)	35
	Cationic resin (Polydiallyldimethyl ammonium chloride, (trademark: PAS-H-10L, made by NITTO BOSEKI K.K.)	15
50	Sodium sulfosalicylate (Chemical reagent grade, made by KANTO KAGAKU K.K.)	5

[0175] The coating liquid had a solid content of 7% by weight.

[0176] The coating liquid was coated on a surface of the resin coated paper sheet by using a die coater, to form an ink receiving layer having a dry weight of 20 g/m². An ink jet recording paper sheet was obtained.

Comparative Example III-1

[0177] An ink jet recording paper sheet was prepared in the same procedures as in Example III-2, except that no

sodium *p*-hydroxybenzenesulfonate was employed.

Comparative Example III-2

- 5 [0178] An ink jet recording paper sheet was prepared in the same procedures as in Example III-2, except that the sodium *p*-hydroxybenzenesulfonate was replaced by tannic acid (chemical reagent grade, made by KANTO KAGAKU K.K.).

Comparative Example III-3

- 10 [0179] An ink jet recording paper sheet was prepared in the same procedures as in Example III-2, except that the sodium *p*-hydroxybenzenesulfonate was replaced by sodium benzenesulfonate (chemical reagent grade, made by KANTO KAGAKU K.K.).

15 TESTS

- [0180] The ink jet recording sheets of the Examples III-1 to III-7 and Comparative Examples III-1 to III-3 were subjected to the tests for evaluating the color density, and light fastness and water resistance of ink images recorded thereon.

- 20 [0181] The tests were carried out by the following methods. In the tests, the recording sheet were printed by using an ink jet printer (trademark: PM-750C, made by EPSON).

(1) Color density of recorded images

- 25 [0182] A solid print was formed with a black-colored ink on each recording sheet, and the color density of the solid print was measured three times by the Macbeth reflection color density tester (model: RD-920, made by Macbeth). An average of the measured color density data was calculated.

(2) Light fastness of recorded images

- 30 [0183] On each recording sheet, ISO-400 images ("High accuracy color digital standard image data, ISO/JIS-SCID", page 13, name of image: Fruit basket, and page 14, name of image: Candle, published by ZAIDANHOGIN NIPPON KIKAKU KYOKAI) in a gloss paper mode, and the printed images was subjected to a continuous fading treatment using a xenon lamp-using FADE-OMETER (model: CI35F, made by ATLAS ELECTRIC DEVICES CO.) at 63°C at 50% RH for 50 hours. The tested images were compared with the original images and evaluated as follows.

40

Class	Tested images
4	Substantially no color-fading is found.
3	Slight color-fading is found. Practically usable.
2	Color is faded to such an extent that color balance is lost. Practically unusable.
1	Color is greatly faded and color balance is significantly lost.

45

50 (3) Water resistant of recorded images

- [0184] After the recorded sheet was left to stand for 24 hours in the ambient atmosphere, a drop of water was placed on the images, and one minute after the placing, the water drop was removed by wiping. The water-wetted portion of the images was observed by the naked eye to evaluate the water resistance of the images as follows.
- 55

Class	Water resistance
3	Substantially no ink in the images was removed.
2	A portion of the ink in the images was removed.
1	The ink images were completely removed.

[0185] The test results are shown in Table 3.

Table 3

Example No.	Item	Recorded ink images		
		color density	Light fastness	Water resistance
Example	III-1	1.29	4	2
	III-2	1.73	4	3
	III-3	2.40	4	3
	III-4	2.35	4	3
	III-5	2.40	3	3
	III-6	2.50	4	3
	III-7	2.45	4	2
Comparative Example	III-1	1.78	1	2
	III-2	1.72	2	3
	III-3	1.70	2	3

[0186] Table 3 clearly shows that the ink jet recording sheet of Examples III-1 to III-7 containing the phenol compounds having at least one sulfonate group enabled the recorded ink images to exhibit a high light fastness. Particularly, the light fastness was very excellent in Examples III-1 to III-4, III-6 and III-7 wherein a phenolsulfonic acid salt or sulfosalicylic acid salt was employed as a phenol compound having at least one sulfonate group. Further, in Examples III-2 to III-6 wherein a pigment and a cationic resin were employed in addition to the light fastness-enhancing agent, the resultant ink jet recording sheet enabled the ink images recorded thereon to exhibit a high color density and a high water resistance. Among them, in Example III-3 to III-6 wherein the pigment comprised fine silica particles having a particle size of 1 μm or less, the recorded ink images exhibited an enhanced sharpness.

[0187] In Comparative Example III-1 wherein no light fastness-enhancing agent was employed, the recorded ink images exhibited a poor light fastness. Also, in Comparative Examples III-2 and III-3 wherein light fastness-enhancing agents other than that of the present invention were used, the resultant ink images exhibited an unsatisfactory light fastness.

Example IV-1

[0188] A trade available PPC paper sheet (a woodfree paper sheet for electrophotograph) was size-pressed with an aqueous size-pressing liquid having the composition shown below and dried, to allow the paper sheet to be impregnated with the size-pressing liquid in a dry weight of 0.5 g/m².

Size-pressing liquid composition	
Component	Part by dry weight
Disodium pyrocatechol-3,5-disulfonate (Tallon, chemical reagent grade, made by KANTO KAGAKU K.K.)	40

(continued)

Size-pressing liquid composition		
	Component	Part by dry weight
5	Calcium chloride (chemical reagent grade, made by KANTO KAGAKU K.K.)	60

[0189] The size-pressing liquid had a solid content of 5% by weight.

[0190] The size-pressed paper sheet was employed as an ink jet recording sheet.

Example IV-2

[0191] A trade available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO., LTD.) having a basis weight of 127.9 g/m² was coated on a surface thereof with a coating liquid having the composition shown below by using a die coater and dried to form an ink receiving layer on the paper sheet. The dry weight of the resultant ink receiving layer was 20 g/m².

Coating liquid composition		
	Component	Part by dry weight
20	Amorphous silica (trademark: FINESIL X-45, made by TOKUYAMA K.K., average agglomerated particle size: 4.5 μm)	100
25	Silyl-modified polyvinyl alcohol (trademark: PVA-R-1130, made by K.K. KURARAY)	35
	Cationic resin (Polydiallyldimethyl ammonium chloride, (trademark: PAS-H-10L, made by NITTO BOSEKI K.K.)	15
30	Sodium p-hydroxybenzenesulfonate (Chemical reagent grade, made by KANTO KAGAKU K.K.)	2
	Calcium chloride (Chemical reagent grade, made by KANTO KAGAKU K.K.)	2

[0192] The coating liquid had a solid content of 7% by weight.

Example IV-3

[0193] An ink jet recording paper sheet was produced by coating a trade-available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO., LTD.) having a basis weight of 127.9 g/m² with a coating liquid having the composition shown below by using a die coater and dried, to form an ink receiving layer having a dry weight of 20 g/m².

Coating liquid composition (total solid content: 7% by weight)		
	Component	Part by dry weight
45	Silica sol IV-A	100
50	Polyvinyl alcohol (trademark: PVA-135H, made by K.K. KURARAY)	35
	Sodium p-hydroxybenzenesulfonate (Chemical reagent grade, made by KANTO KAGAKU K.K.)	8
	Calcium chloride (Chemical reagent grade, made by KANTO KAGAKU K.K.)	8

Preparation of silica sol IV-A

[0194] A synthetic amorphous silica (trademark: NIPSIL HD-2, made by NIPPON SILICA KOGYO K.K.) having a

primary particle size of 11 nm and an average agglomerated particle size of 3 μm was pulverized and dispersed by a sand grinder and then further pulverized and dispersed by a pressure type homogenizer, and the pulverizing and dispersing procedures using the sand grinder and the pressure type homogenizer were repeated until the average agglomerated particle size reached 70 nm, to prepare an aqueous dispersion containing the amorphous silica in a dry content of 8% by weight.

[0195] The aqueous amorphous silica dispersion in an amount of 100 parts by solid weight was mixed with 15 parts by solid weight of a cationic resin comprising of polydiallyldimethyl ammonium chloride (trademark: PAS-H-10L, made by NITTO BOSEKI KOGYO K.K.) to increase the viscosity of the dispersion and then to coagulate the dispersion. The resultant coagulation was pulverized and dispersed by using a sand grinder and further pulverized and dispersed by using a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average particle size reached 490 nm. The resultant aqueous silica sol IV-A had a solid content of 9% by dry weight.

Example IV-4

[0196] An ink jet recording sheet was produced by the following procedures.

[0197] The same coating liquid as in Example IV-3, except that the amount of the sodium *p*-hydroxybenzenesulfonate was changed from 8 parts by weight to 6 parts by weight and the amount of calcium chloride was changed from 8 parts by weight to 6 parts by weight, was coated by using a bar coater on a surface of a casting base consisting of a PET film (trademark: LUMILER T, made by TORAY INDUSTRIES INC.) having a thickness of 50 μm and dried, to form a coating layer having a dry weight of 20 g/m^2 , to form an upper layer of an ink receiving layer.

[0198] The same coating liquid as mentioned above was coated in a solid amount of 10 g/m^2 on a surface of a trade available coated paper sheet (trademark: OK COAT, made by OJI PAPER CO.) having a basis weight of 127.9 g/m^2 , the coated paper sheet was superposed on the coating layer on the PET film surface in a manner such that the coating layer on the paper sheet came into contact with the coating layer on the PET film, the superposed composite was dried and the PET film was peeled off from the resultant ink jet recording sheet.

Example IV-5

[0199] An ink jet recording paper sheet was prepared using the same procedures as in Example IV-3, except that in the preparation of the coating liquid, no sodium *p*-hydroxybenzenesulfonate and no calcium chloride were employed, and after the coating layer formed on the paper sheet, an aqueous solution containing 50 parts by weight of sulfosalicylic acid (chemical reagent grade, made by KANTO KAGAKU K.K.) and 50 parts by weight of magnesium chloride (chemical reagent grade, made by KANTO KAGAKU K.K.) and having a total solid content of 20% by weight, was applied to the coating layer surface and dried, to allow the aqueous solution to be impregnated in a dry weight of 1.0 g/m^2 in the resultant ink jet recording sheet.

Example IV-6

[0200] An ink jet recording paper sheet was prepared in the same procedures as in Example IV-3, except that sodium *p*-hydroxybenzenesulfonate was replaced by hydroquinone (chemical reagent grade, made by KANTO KAGAKU K.K.).

Example IV-7

[0201] An ink jet recording paper sheet was prepared by the following procedures.

[0202] A resin-coated paper sheet for a support sheet was prepared in the following manner.

[0203] An aqueous pulp slurry having a solid content of 0.5% by weight was prepared from a mixture of a soft wood bleached kraft pulp (NBKP) pulped to a Canadian Standard Freeness (CSF) of 300 ml determined in accordance with Japanese Industrial Standard P8121 with a hard wood bleached kraft pulp (LBKP) pulped to a CSF of 350 ml in a mixing weight ratio of 2:8. The pulp slurry was added with 2.0% by weight of a cationic starch, 0.4% by weight of alkylketene dimer, 0.1% by weight of an anionic polyacrylamide resin and 0.7% by weight of a polyamidepolyamine epichlorohydrin resin based on the bone-dried total weight of the pulps in the pulp slurry, and the mixed slurry was fully agitated to uniformly disperse the solid components in the aqueous slurry.

[0204] The aqueous pulp slurry having the above-mentioned composition was subjected to a paper-forming procedure using a Fourdrinier paper machine, a dryer, a size-press, and a machine calender, to produce a paper sheet having a base weight of 180 g/m^2 and a bulk density of 1.0 g/cm^3 . In the sizing procedure, a sizing liquid prepared by heat-dissolving a mixture of a carboxyl-modified polyvinyl alcohol with sodium chloride in a mixing weight ratio of 2:1 in water,

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and having a solid concentration of 5% by weight was applied in an amount of 25 ml to each surface of the paper sheet.

[0205] A corona discharge treatment was applied to both the surfaces of the paper sheet, then a polyolefin resin composition (1) having the composition shown below was coated in an amount of 25 g/m² on the felt side surface of the paper sheet, and a polyolefin resin composition (2) having the composition shown below was coated in an amount of 25 g/m² on the wire side surface of the paper sheet, through T-dies of a melt extruder at a melt temperature of 320°C, and the melt-coated layers were cool-solidified by a mirror-finished peripheral surfaces of cooling rolls, to prepare a support sheet.

Polyolefin resin composition (1)	
Component	Part by dry weight
Long linear low density polyethylene resin (density: 0.926 g/cm ³ , melt index: 20g/10 minutes)	35
Low density polyethylene resin (density: 0.919 g/cm ³ , melt index: 2g/10 minutes)	50
Anatase type titanium dioxide (trademark: A-220, made by ISHIHARA SANGYO K.K.)	15
Zinc Stearate	0.1
Anti-oxidant (trademark: IRGANOX 1010, made by CIBA-GEIGY)	0.03
Ultramarine (BLUISH ULTRAMARINE No. 2000, made by DAIICHI KASEI K.K.)	0.09
Fluorescent brightening agent (trademark: UNITEX OB, made by CIBA-GEIGY)	0.3
Polyolefin resin composition (2)	
Component	Part by dry weight
High density polyethylene resin (density: 0.954 g/cm ³ , melt index: 20g/10 minutes)	65
Low-density polyethylene resin (density: 0.924 g/cm ³ , melt index: 4g/10 minutes)	35
Note: In the polyolefin resin composition (1), the anti-oxidant was employed to prevent the oxidation of the polyethylene resins during the melt-extrusion procedure and the ultramarine and the fluorescent brightening agent were employed to impart a bluing effect and an apparent whitening effect to the resin composition and to improve the naked eye appearance of the resultant coating layer.	

[0206] A coating liquid having the composition shown below was prepared.

Coating liquid composition for ink receiving layer		
Component	Part by dry weight	
Polyvinyl alcohol (trademark: PVA420, made by K.K. KURARAY)	100	
Silyl-modified polyvinyl alcohol (trademark: PVA-R-1130, made by K.K. KURARAY)	35	
Cationic resin (Polydiallyldimethyl ammonium chloride, (trademark: PAS-H-10L, made by NITTO BOSEKI K.K.))	15	
Sodium p-hydroxybenzenesulfonate (Chemical reagent grade, made by KANTO KAGAKU K.K.)	2	

(continued)

Coating liquid composition for ink receiving layer	
Component	Part by dry weight
Sodium dihydrogen phosphate (Chemical reagent grade, made by KANTO KAGAKU K.K.)	2

[0207] The coating liquid had a total solid content of 7%.

[0208] The coating liquid was coated on a surface of the resin coated paper sheet by using a die coater and dried to form an ink receiving layer having a dry weight of 20 g/m².

[0209] An ink jet recording sheet was obtained.

Example IV-8

[0210] An ink jet recording paper sheet was prepared in the same procedures as in Example IV-3, except that, in the preparation of the coating liquid, the sodium *p*-hydroxybenzenesulfonate was replaced by sodium salicylate (chemical reagent grade, made by KANTO KAGAKU K.K.) and calcium chloride was replaced by sodium dihydrogen phosphate.

Comparative Example IV-1

[0211] An ink jet recording paper sheet was prepared in the same procedures as in Example IV-3, except that, in the coating liquid, no sodium *p*-hydroxybenzenesulfonate and no calcium chloride were contained.

Comparative Example IV-2

[0212] An ink jet recording paper sheet was prepared in the same procedures as in Example IV-3, except that, in the coating liquid, no sodium *p*-hydroxybenzenesulfonate was contained and the content of calcium chloride was changed to 16 parts by weight.

Comparative Example IV-3

[0213] An ink jet recording sheet was prepared in the same procedures as in Example IV-3, except that, in the coating liquid, no sodium *p*-hydroxybenzenesulfonate and no calcium chloride were contained and a hindered amine photostabilizer (trademark: TINUBIN 144, made by CIBA-GEIGY) was contained in an amount of 16 parts by weight.

TESTS

[0214] The ink jet recording sheets of the Examples IV-1 to IV-8 and Comparative Examples IV-1 to IV-3 were subjected to the tests for evaluating the color density, light fastness and water resistance of ink images recorded thereon.

[0215] The tests were carried out by the following methods.

[0216] In the tests, the recording sheet were printed by using an ink jet printer (trademark: PM-750C, made by EPSON).

(1) Color density of recorded images

[0217] A solid print was formed with a black-colored ink on each recording sheet, and the color density of the solid print was measured three times by the Macbeth reflection color density tester (model: RD-920, made by Macbeth). An average of the measured color density data was calculated.

(2) Light fastness of recorded images

[0218] On each recording sheet, ISO-400 images ("High accuracy color digital standard image data, ISO/JIS-SCID", page 13, name of image: Fruit basket, and page 14, name of image: Candle, published by ZAIDANHOGIN NIPPON KIKAKU KYOKAI) in a gloss paper mode, and the printed images was subjected to a continuous fading treatment using a xenon lamp-using FADE-OMETER (model: CI35F, made by ATLAS ELECTRIC DEVICES CO.) at 63°C at 50% RH for 50 hours. The tested images were compared with the original images and evaluated as follows.

Class	Tested images
5	Substantially no color-fading is found.
4	Slight color-fading is found.
3	Color is faded and color balance is slightly lost. Practically usable.
2	Color is faded to such an extent that color balance is lost. Practically unusable.
1	Color is greatly faded and color balance is significantly lost.

(3) Water resistant of recorded images

[0219] After the recorded sheet was left to stand for 24 hours in the ambient atmosphere, a drop of water was placed on the images, and one minute after the placing, the water drop was removed by wiping. The water-wetted portion of the images was observed by the naked eye to evaluate the water resistance of the images as follows.

Class	Water resistance
3	Substantially no ink in the images was removed.
2	A portion of the ink in the images was removed.
1	The ink images were completely removed.

[0220] The test results are shown in Table 4.

Table 4

Example No.	Item	Recorded ink images		
		color density	Light fastness	Water resistance
Example	IV-1	1.28	5	2
	IV-2	1.72	4	3
	IV-3	2.20	5	3
	IV-4	2.36	5	3
	IV-5	2.28	5	3
	IV-6	2.18	4	3
	IV-7	2.10	4	2
	IV-8	2.14	3	3
Comparative Example	IV-1	2.35	1	3
	IV-2	2.10	2	3
	IV-3	2.05	2	3

[0221] Table 4 clearly shows that the ink jet recording sheets of Examples IV-1 to IV-8 in which an inorganic salt and a phenol compound are contained, enabled the recorded ink images thereon to exhibit an excellent light fastness. Particularly, on the recording sheets of Examples IV-1 to IV-7 wherein a phenol compound having a sulfonate group and/or an inorganic divalent or more metal salt is contained, the recorded ink images exhibited an excellent light fastness. Also on the recording sheets of Examples IV-2 to IV-8 containing a pigment and a cationic resin in addition to the light fastness-enhancing agent, the recorded ink images exhibited a high color density and a high water resistance.

[0222] Especially, in Examples IV-3 to IV-8 wherein fine silica particles having a particle size of 1 μm were con-

tained as a pigment, the ink images recorded on the resultant recording sheet exhibited a very high color density and sharpness.

[0223] In the recording sheet of Comparative Example IV-1 containing no light fastness-enhancing agent, the recorded ink images exhibited a poor light fastness.

[0224] In the recording sheet of Comparative Example IV-2 containing only an inorganic salt, the recorded ink images exhibited an unsatisfactory light fastness.

[0225] In the recording sheet of Comparative Example IV-3, the light fastness-enhancing effect of the hindered amine photostabilizer for the recorded ink images was insufficient and unsatisfactory.

[0226] In Examples V-1 to V-9 and Comparative Examples V-1 to V-2, the following materials were employed. The materials were prepared by the procedures shown below.

(1) Support sheet V-1

[0227] A support sheet V-1 was prepared by the following procedures.

[0228] An aqueous pulp slurry having a solid content of 0.5% by weight was prepared from a mixture of a soft wood bleached kraft pulp (NBKP) pulped to a Canadian Standard Freeness (CSF) of 300 ml determined in accordance with Japanese Industrial Standard P 8121 with a hard wood bleached kraft pulp (LBKP) pulped to a CSF of 350 ml in a mixing weight ratio of 2:8. The pulp slurry was added with 2.0% by weight of a cationic starch, 0.4% by weight of alkylketene dimer, 0.1% by weight of anionic polyacrylamide resin and 0.7% by weight of a polyamidepolyamine epichlorohydrin resin based on the bone-dry total weight of the pulps in the pulp slurry, and the mixed slurry was fully agitated to uniformly disperse the solid components in the aqueous slurry.

[0229] The aqueous pulp slurry having the above-mentioned composition was subjected to a paper-forming procedure using a Fourdrinier paper machine, a dryer, a size-press, and a machine calender, to produce a paper sheet having a base weight of 157 g/m² and a bulk density of 1.0 g/cm³. In the sizing procedure, a sizing liquid prepared by heat-dissolving a mixture of a carboxyl-modified polyvinyl alcohol with sodium chloride in a mixing weight ratio of 2:1 in water, and having a solid concentration of 5% by weight was applied in a total amount of 25 ml to both the surfaces of the paper sheet.

[0230] A support paper sheet V-1 was obtained.

(2) Support sheet V-2

[0231] To both the surfaces of the support paper sheet V-1, a corona discharge treatment was applied, then a polyolefin resin composition (1) (a front layer-forming resin composition) having the composition shown below and prepared by mixing and dispersing with a Bumbury's mixer was coated in an amount of 25 g/m² on the felt side surface of the paper sheet, and a polyolefin resin composition (2) (a back layer-forming resin composition) having the composition shown below and prepared by mixing and dispersing with a Bumbury's mixer was coated in an amount of 20 g/m² on the wire side surface of the paper sheet, through T-dies of a melt extruder at a melt temperature of 320°C, and the melt-coated layers were cool-solidified on mirror-finished peripheral surfaces of cooling rolls, to prepare a support sheet.

Polyolefin resin composition (1)	
Component	Part by dry weight
Long linear low density polyethylene resin (density: 0.926 g/cm ³ , melt index: 20g/10 minutes)	35
Low density polyethylene resin (density: 0.919 g/cm ³ , melt index: 2g/10 minutes)	50
Anatase type titanium dioxide (trademark: A-220, made by ISHIHARA SANGYO K.K.)	15
Zinc Stearate	0.1
Anti-oxidant (trademark: IRGANOX 1010, made by CIBA-GEIGY)	0.03
Ultramarine (BLUISH ULTRAMARINE No. 2000, made by DAIICHI KASEI K.K.)	0.09
Fluorescent brightening agent (trademark: UNITEX OB, made by CIBA-GEIGY)	0.3
Polyolefin resin composition (2)	
Component	Part by dry weight
High density polyethylene resin (density: 0.954 g/cm ³ , melt index: 20g/10 minutes)	65
Low density polyethylene resin (density: 0.924 g/cm ³ , melt index: 4g/10 minutes)	35
Note: In the polyolefin resin composition (1), the anti-oxidant was employed to prevent the oxidation of the polyethylene resins during the melt-extrusion procedure and the ultramarine and the fluorescent brightening agent were employed to impart a bluing effect and apparent whitening effect to the resin composition and to improve the appearance of the resultant coating layer, when observed by the naked eye.	

(3) Silica sol V-A

[0232] A synthetic amorphous silica (trademark: NIPSIL HD-2, made by NIPPON SILICA KOGYO K.K.) having a primary particle size of 11 nm and an average agglomerated particle size of 3 μ m was pulverized and dispersed by a sand grinder and then further pulverized and dispersed by a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average agglomerated (secondary) particle size reached 500 nm, to prepare an aqueous dispersion containing the amorphous silica in a dry content of 8% by weight.

[0233] When the aqueous amorphous silica dispersion in an amount of 100 parts by solid weight was mixed with 15 parts by solid weight of a cationic resin comprising of polydiallyldimethyl ammonium chloride (trademark: PAS-H-10L, made by NITTO BOSEKI KOGYO K.K.), the particle size of the agglomerated particles were increased, the viscosity of the dispersion was increased and then the dispersion was coagulated. The resultant coagulation was pulverized and dispersed by using a sand grinder and further pulverized and dispersed by using a pressure type homogenizer, and the pulverizing and dispersing procedures by the sand grinder and the pressure type homogenizer were repeated until the average particle size reached 150 nm. The resultant aqueous dispersion had a solid content of 9% by dry weight.

(4) Silica sol V-B

[0234] A synthetic amorphous silica (trademark: NIPSIL-LP, made by NIPPON SHIRICA KOGYO K.K.) comprising a plurality of agglomerated (secondary) particles having an average particles size of 3 μ m and each consisting of a plurality of primary particles having a primary particle size of 16 nm and agglomerated with each other was pulverized and dispersed by using a sand grinder and then further pulverized and dispersed by using a pressure type homogenizer,

and the pulverize-dispersing procedures by using the sand grinder and then, by using the pressure type homogenizer were repeated until the average particle size of the agglomerated (secondary) particles reached 500 nm. The resultant aqueous silica dispersion had a solid content of 9% by weight.

5 Example V-1

[0235] An aqueous coating liquid was prepared by dissolving 100 parts by weight of a polyvinyl alcohol (trademark: PVA-224, made by KURARAY K.K.) having a degree of polymerization of 2400 and a degree of saponification of 88% and mixed with 10 parts by weight of a cationic resin (polydiallyldimethyl ammonium chloride, trademark: PAS-H-10L, made by NITTO BOSEKI K.K.), 5 parts by weight of sodium metaphosphate (made by KANTO KAGAKU K.K.) and 10 parts by weight of disodium pyrocatechol-3,5-disulfonate, in water.

[0236] The coating liquid was coated on a surface of the support sheet V-2 and dried to form an ink receiving layer in a dry weight of 10 g/m².

[0237] An ink jet recording material of the present invention was obtained.

15 Example V-2

[0238] An aqueous coating liquid was prepared by mixing 100 parts by weight of the Silica sol V-A with 35 parts by weight of a polyvinyl alcohol (trademark: PVA-135H, made by KURARAY K.K.) having a degree of polymerization of 3500 and a degree of saponification of 99% or more, 5 parts by weight of sodium dihydrogen phosphate dihydrate (made by KANTO KAGAKU K.K.), 10 parts by weight of a cationic resin (polydiallyldimethyl ammonium chloride, trademark: PAS-H-10L, made by NITTO BOSEKI K.K.), and 5 parts by weight of hydroquinone- β -D-glucoside (made by KANTO KAGAKU K.K.). The aqueous coating liquid had a solid content of 7% by weight.

[0239] The coating liquid was coated on a surface of the support sheet V-2 and dried to form an ink receiving layer in a dry weight of 20 g/m².

[0240] An ink jet recording material of the present invention was obtained.

Example V-3

30 [0241] An aqueous coating liquid was prepared by mixing 100 parts by weight of the silica sol V-A with 30 parts by weight of a polyvinyl alcohol (trademark: PVA-104H, made by KURARAY K.K.) having a degree of polymerization of 4000 and a degree of saponification of 99% or more, and 10 parts by weight of a cationic resin (polydiallyldimethyl ammonium chloride, trademark: PAS-H-10L, made by NITTO BOSEKI K.K.) and 5 parts by weight of sodium metaphosphate (made by KANTO KAGAKU K.K.). The coating liquid had a solid content of 8% by weight.

35 [0242] The coating liquid was coated on a surface of a casting base consisting of a PET film (trademark: LUMILER T, made by TORAY INDUSTRIES INC.) having a thickness of 38 μ m and a Ra of 0.02 μ m, and dried, to form a coating layer having a dry weight of 10 g/m². The coating layer was coated with a 15% by weight aqueous solution containing 100 parts by weight of sodium phenolsulfonate and 60 parts by weight of sodium dihydrogen phosphate dihydrate and dried, to cause the sodium phenolsulfonate and the sodium dihydrogen phosphate dihydrate to be contained in a dry weight of 1.5 g/m² in the coating layer and to form an upper layer of an ink receiving layer.

40 [0243] An aqueous coating liquid containing, in a solid content of 8% by weight, 35 parts by weight of polyvinyl alcohol (trademark: PVA-140H, made by KURARAY K.K.) and 100 parts by weight of the silica sol V-B was coated in a solid amount of 15 g/m² on a surface of the support sheet V-1, the coated paper sheet was superposed on the coating layer on the PET film surface in a manner such that the coating layer on the paper sheet came into contact with the coating layer on the PET film, the superposed composite was dried, and the PET film was peeled off from the resultant ink jet recording sheet.

Example V-4

50 [0244] An ink jet recording material was produced by the same procedures as in Example V-3, except that the sodium dihydrogen phosphate dihydrate was replaced by sodium triphosphate.

Example V-5

55 [0245] An ink jet recording material was produced by the same procedures as in Example V-3, except that the sodium dihydrogen phosphate dihydrate was replaced by sodium diphosphate.

Example V-6

[0246] An ink jet recording material was produced by the same procedures as in Example V-3, except that the sodium dihydrogen phosphate dihydrate was replaced by calcium glycerophosphate.

Example V-7

[0247] An ink jet recording material was produced by the same procedures as in Example V-3, except that the sodium dihydrogen phosphate dihydrate was replaced by hydrogen disodium phosphate.

Example V-8

[0248] An ink jet recording material was produced by the same procedures as in Example V-3, except that the sodium dihydrogen phosphate dihydrate was replaced by sodium nitrate.

Example V-9

[0249] An aqueous coating liquid was prepared by mixing 100 parts by weight of the silica sol V-A with 30 parts by weight of polyvinyl alcohol (trademark: PVA-104H, made by KURARAY K.K.) and 10 parts by weight of a cationic resin (polydiallyldimethyl ammonium chloride, trademark: PAS-H-10L, made by NITTO BOSEKI K.K.). The coating liquid had a solid content of 8% by weight.

[0250] The coating liquid was coated on a surface of a casting base consisting of a PET film (trademark: LUMILER T, made by TORAY INDUSTRIES INC.) having a thickness of 38 μm and a Ra of 0.02 μm , and dried, to form a coating layer having a dry weight of 10 g/m². The coating layer was coated with a 15% by weight aqueous solution containing 100 parts by weight of sodium phenolsulfonate and 60 parts by weight of sodium dihydrogen phosphate dihydrate and dried, to cause the sodium phenolsulfonate and the sodium dihydrogen phosphate dihydrate to be contained in a dry weight of 1.5 g/m² in the coating layer and to form an upper layer of an ink receiving layer.

[0251] An aqueous coating liquid containing, in a solid content of 8% by weight, 100 parts by weight of the silica sol V-B, 35 parts by weight of polyvinyl alcohol (trademark: PVA-140H, made by KURARAY K.K.), and 10 parts by weight of a cerium oxide sol (trademark: U-15, made by TAKI KAGAKU K.K.) was coated in a solid amount of 15 g/m² on a surface of the support sheet V-1, the coated paper sheet was superposed on the coating layer on the PET film surface in a manner such that the coating layer on the paper sheet came into contact with the coating layer on the PET film, the superposed composite was dried, and the PET film was peeled off from the resultant ink jet recording sheet.

Comparative Example V-1

[0252] An ink jet recording material was produced by the same procedures as in Example V-1, except that no disodium pyrocatechol-3,5-disulfonate was employed for the ink receiving layer.

Comparative Example V-2

[0253] An ink jet recording material was produced by the same procedures as in Example V-2, except that no sodium dihydrogen phosphate dihydrate and no hydroquinone- β -D-glucoside were employed.

TESTS

[0254] The ink jet recording materials of the Examples V-1 to V-9 and Comparative Examples V-1 to V-2 were subjected to the tests for evaluating the water resistance and gloss of coated layer, the color density, and light fastness of ink images recorded thereon, and the ink absorption of the recording materials.

[0255] The tests were carried out by the following methods.

[0256] In the tests, the recording sheet were printed by using an ink jet printer (trademark: PM-700C, made by EPSON).

(1) Water resistance of coated layer

[0257] A drop of water was placed on a ink receiving layer of the ink jet recording material. One minute after the water drop was placed, the water drop was removed by wiping. The water-wetted portion of the ink jet recording material were observed by the naked eye to evaluate the water resistance of the coated layer of the recording material, as

follows

Class	Water resistance
3	No change is found on the coated layer
2	The coated layer or a portion of the coated layer is swollen. Practically usable.
1	The coated layer is completely removed.

(2) Color density of recorded images

[0258] A solid print was formed with a black-colored ink on each recording sheet, and the color density of the solid print was measured three times by the Macbeth reflection color density tester (model: RD-920, made by Macbeth). An average of the measured color density data was calculated.

(3) Gloss

[0259] A gloss of the ink jet recording surface was measured in accordance with Japanese Industrial Standard (JIS) Z 8741, 75 degrees mirror-finished surface gloss, by using a gloss meter (made by NIPPON DENSHOKUKOGYO K.K.).

(4) Light fastness of recorded images

[0260] On each recording sheet, ISO-400 images ("High accuracy color digital standard image data, ISO/JIS-SCID", page 13, name of image: Fruit basket, and page 14, name of image: Candle, published by ZAIDANHOGIN NIPPON KIKAKU KYOKAI) in a gloss paper mode, and the printed images was subjected to a continuous fading treatment using a xenon lamp-using FADE-OMETER (model: CI35F, made by ATLAS ELECTRIC DEVICES CO.) at 63°C at 50% RH for 20 hours (at an accumulated energy amount of light at 420 nm of 40.5 kJ/m²). The tested images were compared with the original images and evaluated as follows.

Class	Tested images
4	Substantially no color-fading is found.
3	Slight color-fading is found.
2	Color is faded.
1	Color is greatly faded.

(5) Ink absorption

[0261] The ink jet recording material was subjected to a 100% solid printing with a recording density of 720 dpi using the above-mentioned ink jet printer.

[0262] A PPC paper sheet was placed on the printed portion of the recording material. The time needed for the ink on the printed portion of the recording sheet to be completely absorbed in the recording material, and thus not transferred onto the PPC paper sheet, was determined.

[0263] The ink absorption of the recording material was evaluated as follows

Class	Ink absorbing time
4	Less than 10 seconds
3	10 seconds or more but less than 2 minutes

(continued)

Class	Ink absorbing time
2	2 minutes or more but less than 10 minutes
1	10 minutes or more. Useless for practice

[0264] The test results are shown in Table 5.

Table 5

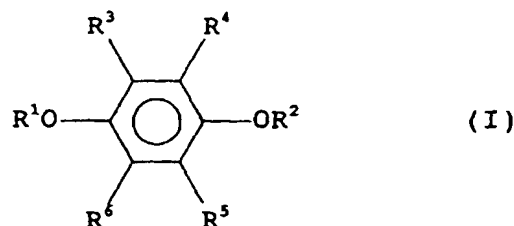
Example No.	Item	Water resistance of coated layer	Gloss at 75 degree angle	Color density of images	Light fastness of images	Ink absorption
Example	V-1	△	97	2.65	4	2
	V-2	○	39	2.40	4	4
	V-3	○	70	2.52	4	4
	V-4	○	65	2.48	3	4
	V-5	○	69	2.50	3	4
	V-6	○	69	2.50	4	4
	V-7	○	67	2.45	3	4
	V-8	○	67	2.48	3	4
	V-9	○	68	2.45	4	4
Comparative Example	V-1	△	90	2.60	2	2
	V-2	○	42	2.35	1	4

[0265] Table 5 clearly shows that the ink jet recording materials of Examples V-1 to V-9 in accordance of the present invention exhibited a high water resistance of coated layers, a high color density of recorded images, a high gloss of the recording material and an excellent light fastness of the recorded images.

[0266] The ink jet recording material of the present invention enables the ink images recorded thereon to exhibit a significantly enhanced resistance to light fading.

Claims

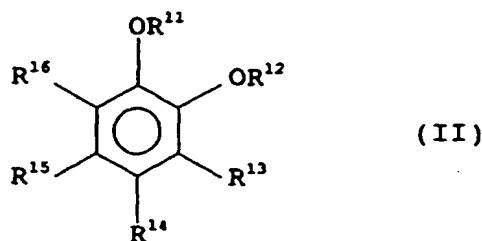
1. An ink jet recording material comprising a support material and a light fastness-enhancing agent for ink images received on the recording material, the light fastness-enhancing agent being comprised in or on the support material, and comprising at least one member selected from the group consisting of hydroquinone, hydroquinone derivatives, pyrocatechol derivatives and phenol compounds having at least one sulfonate group.
2. The ink jet recording material as claimed in claim 1, wherein the light fastness-enhancing agent comprises at least one member selected from the group consisting of hydroquinone and hydroquinone derivatives.
3. The ink jet recording material as claimed in claim 1, wherein the hydroquinone derivatives are selected from those represented by the general formula (I):



15 wherein R¹ and R² respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups, and -R⁷-COOH groups wherein R⁷ represents a hydrocarbon group; R³, R⁴, R⁵ and R⁶ respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a sulfonic acid group, a sulfonate salt group, a carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups and aralkyl groups, and R³ and R⁴ and R⁵ and R⁶ respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; at least one of R¹ to R⁶ is not a hydrogen atom; and the saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups and -R-COOH groups represented by R¹ to R² and the alkyl groups, aryl groups and aralkyl groups represented by R³, R⁴, R⁵ and R⁶ each may have at least one substituent.

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4. The ink jet recording material as claimed in claim 2, wherein the light fastness-enhancing agent comprises, as a hydroquinone derivative, hydroquinone-β-D-glucoside.
 5. The ink jet recording material as claimed in claim 1, wherein the light fastness-enhancing agent comprises at least one member selected from pyrocatechol derivatives.
 6. The ink jet recording material as claimed in claim 1, wherein the pyrocatechol derivatives are selected from those represented by the general formula (II):
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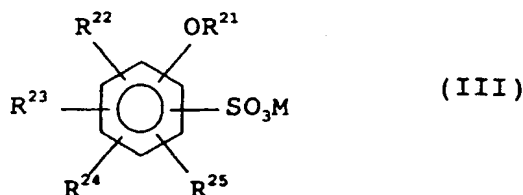
45 wherein R¹¹ and R¹² respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups, and -R¹⁷-COOH groups wherein R¹⁷ represents a hydrocarbon group; R¹³, R¹⁴, R¹⁵ and R¹⁶ respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a sulfonic acid group, a sulfonate salt group, a carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups and aralkyl groups, and R¹³ and R¹⁴ and R¹⁵ and R¹⁶ respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; and the saccharose residues, aryl groups, acyl groups, aralkyl groups, alkyl groups and -R-COOH groups represented by R¹¹ to R¹² and the alkyl groups, aryl groups and aralkyl groups represented by R¹³, R¹⁴, R¹⁵ and R¹⁶ each may have at least one substituent.

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7. The ink jet recording material as claimed in claim 5 or 6, wherein the pyrocatechol derivative for the light fastness-enhancing agent is selected from salts of pyrocatechol-3,5-disulfonic acid.
 8. The ink jet recording material as claimed in claim 5, wherein the salts of pyrocatechol-3,5-disulfonic acid include disodium pyrocatechol-3,5-disulfonate.
 9. The ink jet recording material as claimed in claim 1, wherein the light fastness-enhancing agent comprises at least
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one member selected from phenol compounds having at least one sulfonate group.

10. The ink jet recording material as claimed in claim 1, wherein the phenol compounds having at least one sulfonate group ($-\text{SO}_3-$) are selected from those represented by the general formula (III):



wherein R^{21} represents a member selected from the group consisting of a hydrogen atom, saccharose residues, aryl groups, acyl groups, aralkyl groups and alkyl groups; R^{22} , R^{23} , R^{24} and R^{25} respectively and independently from each other represent a member selected from the group consisting of a hydrogen atom, a hydroxyl group, $-\text{SO}_3\text{M}$ groups, a carboxylic acid group, carboxylate salt groups, alkyl groups, aryl groups and aralkyl groups; R^{22} and R^{23} and R^{24} and R^{25} respectively and independently from each other may be cyclized together to form a cyclic hydrocarbon group; the saccharose residues, aryl groups, acyl groups, aralkyl groups and alkyl groups represented by R^{21} and the alkyl groups, aryl group and aralkyl group may have at least one substituent; M represents a member selected from the group consisting of a hydrogen atom, metal atoms, an ammonium group and cationic organic groups.

11. The ink jet recording material as claimed in claim 9 or 10, wherein the phenol compounds having at least one sulfonate group are selected from salts of phenol sulfonic acid and salts of sulfosalicylic acid.

12. The ink jet recording material as claimed in claim 1, wherein the light fastness-enhancing agent is impregnated, in the state of an impregnation liquid containing it, in the support material and dried; or is coated, in the state of a coating liquid containing it, on the support material and dried.

13. The ink jet recording material as claimed in claim 12, wherein the impregnation or coating liquid further contains at least one member selected from the group consisting of cationic resins and non-cationic resins.

14. The ink jet recording material as claimed in claim 12, wherein the impregnation or coating liquid further contains at least one inorganic pigment.

15. The ink jet recording material as claimed in claim 1, wherein an ink receiving layer comprising the light fastness-enhancing agent and a pigment is formed on at least one surface of the support material.

16. The ink jet recording material as claimed in claim 15, wherein the pigment is selected from inorganic pigments comprising a plurality of fine inorganic particles having an average particle size of $1\text{ }\mu\text{m}$ or less.

17. The ink jet recording material as claimed in claim 1, wherein an ink receiving layer containing the light fastness-enhancing agent is formed on the support material in such a manner that a layer containing the light fastness-enhancing agent is formed on a casting surface of a casting base, and then is brought into contact with a surface of the support material under pressure so as to transfer the cast layer to the support material surface, and the cast layer on the support material is separated from the casting surface of the casting base.

18. The ink jet recording material as claimed in claim 14 or 16, wherein the inorganic pigment comprises a plurality of particles of at least one member selected from the group consisting of silica, alumina and aluminosilicate.

19. The ink jet recording material as claimed in claim 16, wherein the inorganic pigment comprises a plurality of secondary particles having an average particle size of 10 to 500 nm, each secondary particle comprising a plurality of primary particles having an average primary particle size of 3 to 40 nm, and agglomerated with each other to form the secondary particle.

20. The ink jet recording material as claimed in claim 1, having a gloss of 20% or more determined at incident and

reflection angles of 75 degrees in accordance with Japanese Industrial Standard P8142.

21. The ink jet recording material as claimed in claim 1, further comprising at least one inorganic salt.

5 22. The ink jet recording material as claimed in claim 21, wherein the inorganic salt is selected from salts of di- or more valent metals.

23. The ink jet recording material as claimed in claim 22, wherein the di- or more valent metal salts are selected from the group consisting of magnesium salts and calcium salts.

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24. The ink jet recording material as claimed in claim 1, further comprising at least one member selected from the group consisting of salts of phosphoric acid and salts of nitric acid.

25. The ink jet recording material as claimed in claim 24, wherein the phosphoric acid salts are selected from the group consisting of salts of glycerophosphoric acid and metaphosphoric acid.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 30 1183

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Place of search THE HAGUE		Date of completion of the search 4 May 2000	Examiner Bacon, A
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EUROPEAN SEARCH REPORT

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